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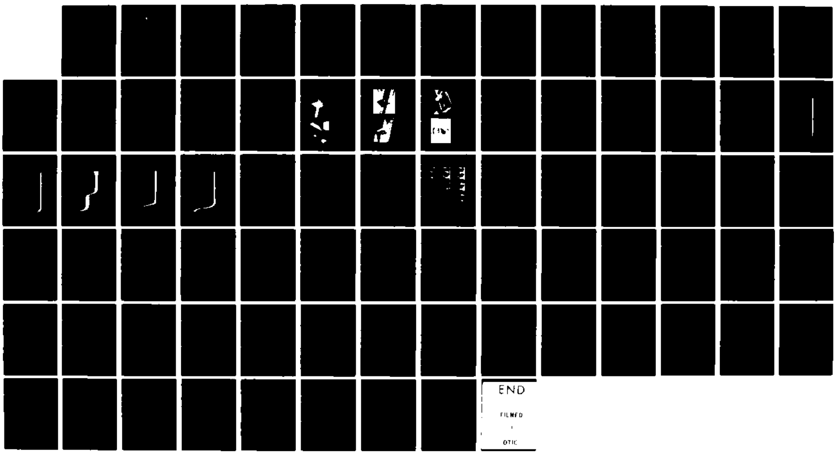

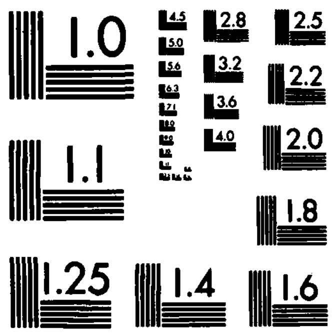

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THE DISPLACEMENT OF WATER FROM A STEEL SURFACE

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8 November 1982

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A quantitative test to evaluate liquid compounds for their ability to displace water droplets from a steel surface has been developed and a study of the water displacement mechanism has been made. The test method consists of placing water droplets onto an inclined steel surface, followed by the application of a test agent. The agent flows down the surface, contacting the water drops. The water may either remain on the specimen or be displaced. The specimen is then immersed in methanol which absorbs residual water on the specimen. The menthanol is then analyzed for water content, yielding a

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20. Abstract (Continued)

quantitative result for water displacement.

Five materials have been evaluated. Two silicone alkyd compounds were found to be good water displacers. A third silicone alkyd compound was found to be a poor displacer at low angles but effective at higher angles. An acrylic and an epoxy coating were found to be poor water displacers.

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INTRODUCTION

Water displacement is defined as the removal of macroscopic quantities of water from a metal surface by the application of a liquid compound. The objective of this displacement is to reduce the risk of corrosion. A situation requiring the displacement of water is the cleaning and preserving of metallic equipment following water immersion. Another example is the painting of metals susceptible to corrosion in a marine environment.

Early investigations of water displacement were performed to develop cleaning and preservation materials for salvaged naval equipment, references (d) through (i). In these efforts, removal of continuous layers or puddles of water was a significant problem and many materials were evaluated for their ability to displace water, reference (d).

A mechanism for the displacement of a continuous water layer from a surface by organic compounds has been described, references (a) and (i). The displacing agent is dropped onto the water layer. Upon impact, a two-dimensional spreading pressure is formed at the agent-water interface. This pressure causes the lateral transportation of water from the impact site and allows penetration of the agent into the water phase. Spreading pressure has been described by the following relationship, reference (f):

$$F_{aw} = (\gamma_w - \gamma_a) - \gamma_{aw} \qquad (1)$$

where: F_{aw} = spreading pressure (dynes per centimeter)

γ_w = surface tension of the water (dynes per centimeter)

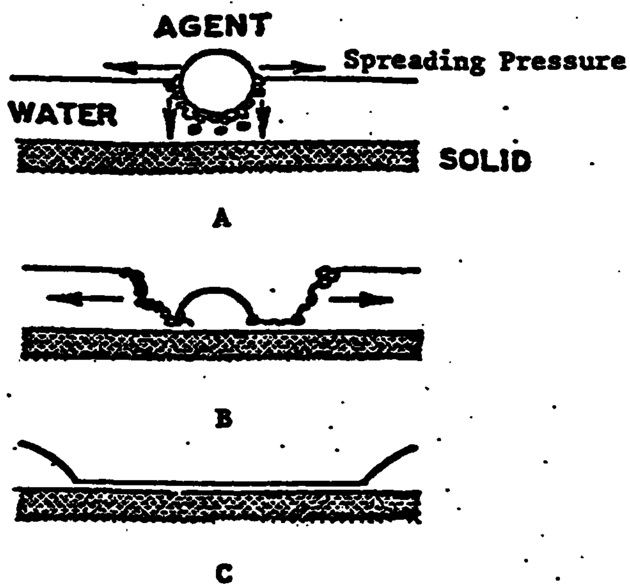
γ_a = surface tension of the displacing agent (dynes per centimeter)

γ_{aw} = interfacial surface tension between water and the agent (dynes per centimeter)

Being slightly soluble in water (usually between 2 and 25 weight percent), the agent diffuses to the metal surface. By preferential adsorption, the agent adheres to the surface and displaces the water layer from the metal substrate. Figure 1 illustrates this mechanism.

The following properties are required of an agent for it to successfully displace a continuous water layer, reference (i):

1. A surface tension which is significantly lower than the water layer.
2. Moderate solubility in water.
3. Moderate volatility.
4. Low viscosity.



A. Displacing agent applied to water surface, spreading pressure and mixing with water begins.

B. Agent reaches the surface while pushing water aside.

C. Preferential adsorption of the agent onto the surface causes water to be displaced.

Figure 1. Mechanism of Water Displacement - Continuous Phase, Reference (i)

The alcohols, especially 1-butanol, have been found to facilitate the above mechanism because of their conformance with the required properties and their amphipathic nature. The polar end of the alcohol allows the compound to preferentially adsorb onto the metal by forming secondary bonds with the surface.

The above efforts were based on the requirement that a continuous phase of water, a puddle, had to be displaced. The phenomenon discussed in this report, however, is the displacement of a discontinuous water phase, water droplets, from a metal surface. This is encountered when painting metal surfaces in a marine environment. The metal is readily susceptible to the formation of water condensates and spray which will form as droplets on the surface. Corrosion control procedures must insure removal of this water. This can be accomplished using water displacing compounds.

A mechanism has been proposed for displacing a discontinuous water phase from a metal surface, reference (k). This mechanism requires the displacing agent to:

1. Spread over the metal surface upon application, wetting the substrate and contacting the water droplets.

2. Be immiscible with water to ensure no water entrapment in the displacing agent.

3. Have a higher affinity for the substrate than water in order for the agent to diffuse under the droplets and thus displace them from the surface.

The difference between the two displacement mechanisms described is the spreading pressure and water miscibility requirements. Impact, dissolution, and diffusion are the only means by which displacing agents can reach the metal surface when displacing a continuous phase. These are unnecessary when displacing droplets because the agents can make direct contact with the surface without mixing with the water. In this case, the controlling factors are agent wettability and preferential adsorption on the metal surface.

There are several tests which have been designed to determine the ability of a material to displace water, references (a), (d), (l), (m), (n), and (o). Table I lists the tests and a brief description of the methods. Most of these methods are qualitative, with the results obtained from an estimated extent of substrate corrosion caused by water remaining on the metal surface. The more extensive the corrosion, the less efficient the material as a water displacer. These tests do not lend themselves to quantitative evaluation of the water displacing phenomenon. Only one of these tests is quantitative, references (a) and (d), and it is designed to test the displacement of a continuous water layer. It is not applicable to evaluation of discontinuous water layers.

The objective of this effort has been to devise and validate a quantitative test for the displacement of a discontinuous phase of water on a steel surface.

Table I. Water Displacement Tests

TEST	METHOD
Continuous water layer, references (a) and (d)	A thin continuous layer of water is placed onto a steel specimen. A droplet of test agent is dropped onto the water and the circumference of the resulting impression in the water layer which the agent makes upon contact is estimated. Reproducibility of this test is claimed to be ±10%.
Static water drop, reference (1)	A drop of water is introduced onto a flat steel specimen containing a conical depression. The test agent is applied. The specimen is then periodically examined for corrosion products in the depression.
Partial water immersion, reference (m)	A steel specimen is immersed in the displacing agent and then immersed in water. The specimen is periodically examined for corrosion.
Water spray test, reference (1)	A steel specimen is immersed in the agent for one hour and then suspended in a humidity cabinet. The specimen is periodically examined for corrosion.
Oil Test, reference (n)	A steel specimen is immersed in a constantly stirred mixture of 10% water in oil. The specimen is periodically examined for corrosion.
Water droplets, reference (o)	Water droplets are introduced onto a steel specimen after which a test agent is applied and allowed to flow over the specimen. The specimen is then placed in a 100% relative humidity chamber. The specimen is periodically examined for corrosion.

The test was designed as a means of evaluating materials for their water displacing ability and as a research tool to assist future investigation of water displacement. Also, several compounds were tested and the results will be discussed in light of the proposed displacement mechanism.

This work was performed under AIRTASK WF61-564-001, Work Unit Number ZM501.

EXPERIMENTAL

The objective of devising a water displacement test is to provide a quantitative means of evaluating compounds for this property. The method which has been devised includes the placement of water droplets onto a steel surface followed by the application of the test agent onto that surface. The specimen is then immersed in methanol. The residual water mixes with the methanol and the solution is quantitatively analyzed for water content. This result will indicate the quantity of water displaced.

MATERIALS

AISI 1010 steel specimens of dimensions 2 x 4 x 0.125 in. (5.1 x 10.2 x 0.32 cm) were used for the metallic substrate. The specimen preparation procedures are listed in Table II.

Distilled water was used for the test. The water droplets applied to the steel surface were 25 microliters in volume. Various properties of the water and water droplets are listed in Table III.

Reagent grade methanol was stored in air-tight containers until used. The initial water content of the methanol was determined during the procedure and will be described later in this section.

Table IV lists the test agents evaluated for water displacing ability. Appendix A lists the specific compositions of these compounds. These materials were investigated because of the wide range of water displacing ability which they exhibited in preliminary studies using the water drop test, reference (o).

The silicone alkyd compounds coded SA-1 and SA-2 in Table IV are known for their water displacing ability, references (k), (o), and (p). SA-3 has the same composition as SA-2 but without petroleum sulfonate. The epoxy ester, EE-1, and acrylic, AC-1, formulations are poor water displacers.

TEST APPARATUS

A specimen holder was designed and fabricated to hold specimens at angles ranging from 5 to 85 degrees in increments of 5 degrees. Machining tolerances were requested to be within 30 minutes. Confirmation of the specimen angles was performed by measuring the angle with a calibrated protractor. The specimen slots were found to be within one degree of the specified angle.

Table II. Method of Specimen Preparation

Specimens used: 5.1 by 10.2 by 0.32 centimeters, AISI 1010 steel

STEP	PROCESS
1	Grind the surface of the specimen to a roughness of 0.432 ± 0.127 root mean square micrometers (a).
2	Immerse the specimen in boiling mineral spirits (b) for ten minutes.
3	Immerse the specimen in a second container of boiling mineral spirits.
4	Slowly immerse the specimen into a boiling solution of 90% reagent grade methanol and 10% distilled water.
5	Immerse the specimen into boiling 100% reagent grade methanol.
6	Store the specimen in a dry desicator at room temperature until testing.

(a) The specimens were purchased in this condition from Metaspec Company. The roughness was measured using a profileometer.

(b) Mineral spirits conforming to Federal Specification TT-T-291.

Table III. Water Drop Properties

Volume: 25.07 ± 0.16 microliters

Weight: 25.07 ± 0.16 milligrams

Height of drop on specimen: 2.06 ± 0.04 millimeters

Shape of drop on specimen: Due to surface grooves caused by polishing, the drops on the specimen were oblong, forming an ellipse. The length of the ellipse was in the direction of the grooves, which were in the length direction of the specimen. Preliminary studies confirmed the direction of the grooves had no effect on the water displacing ability of a compound.

Length of Ellipse:
5.54 ± 0.12 millimeters

Width of Ellipse:
4.17 ± 0.14 millimeters

Contact angle of the drop on the specimen (a): 85 degrees

Surface tension of the water (b): 72.8 dynes per centimeter

(a) Measured by observing a drop from a side angle at a magnification of 50x.

(b) Measured according to ASTM method D-1331, which is the ring method for measuring surface tension.

Table IV. Compounds Evaluated for Water Displacement Ability

CODE	DESCRIPTION
SA-1 (Silicone Alkyd)	A silicone alkyd/silicone binder coating with barium petroleum sulfonate and organic solvents.
SA-2	A silicone alkyd binder paint with petroleum sulfonate, an organo-titanate, pigments, and organic solvents.
SA-3	The same as SA-2 without petroleum sulfonate.
AC-1 (Acrylic)	A poly(methylmethacrylate) binder paint with a commercial plasticizer, pigments, and organic solvents.
EE-1 (Epoxy Ester)	An epoxy ester resin thinned with xylene.

See Appendix A for the specific compositions of these materials.

A microsyringe was used to apply the 25 microliter water droplets. The syringe was calibrated by measuring six droplets individually using an analytical balance. The average drop weight was 25.07 milligrams with a standard deviation of 0.16 milligrams, indicating a drop volume of 25.07 $\pm$ 0.16 microliters.

Half-liter jars with an inner diameter of 6.35 centimeters and a height of 15.35 centimeters were used to immerse the specimens during the procedure. Each jar was sealed by placing aluminum foil between the jar head and the lid. To confirm that the jars were sealed from atmospheric water, 350 milliliters of methanol were placed in each of six sealed jars. The water content of the methanol was determined before and after a 24 hour period using a Karl-Fisher titration technique specified in ASTM method D-890, reference (q), and described later in this report. No significant increase in water content was found.

The Karl-Fisher titrations were performed using an Aquatest IV aquameter manufactured by Photovolt Corporation. The instrument was calibrated daily by titrating 10 microliters of water.

TEST PROCEDURE

The Test Procedures and Equipment are illustrated in Figures 2 through 7. A specimen was placed at the desired angle in the specimen holder. The holder was then inclined such that the appropriate surface of the specimen was horizontal and facing upward. Using the microsyringe, six 25 microliter drops of water were applied to the specimen, Figure 2. Six drops are the maximum amount possible without the drops interfering with each other during the displacing action. After application, the specimen holder was slowly lowered until the specimen was at the desired angle, Figure 3. The drops were applied in this manner to maintain consistancy in transferring the drops from the syringe to the substrate. When lowered to the appropriate angle, and prior to agent application, the drops remained on the specimens at all angles for all specimens tested.

It was determined that one milliliter of test agent would be adequate to cover the entire specimen without excess agent. With the drops in place and the specimen at the correct angle, one milliliter of the test agent was applied along the upper edge of the specimen using a standard two milliliter syringe, Figure 4. Minimal pressure was applied to the plunger of the syringe to minimize momentum of the agent flowing down the specimen. In this manner, the agent could flow down the panel and contact the droplets. The droplets could then flow down and off of specimen thus being displaced. During the test, displaced droplets would often gather at the bottom edge of the specimen, therefore a cotton swab was guided along this edge to absorb and remove any displaced water which may have gathered, Figure 5.

At this time, the specimen was removed from the holder and placed in an air-tight jar containing 350 milliliters of reagent grade methanol such that the specimen was completely immersed in the methanol, Figure 2, Part E.

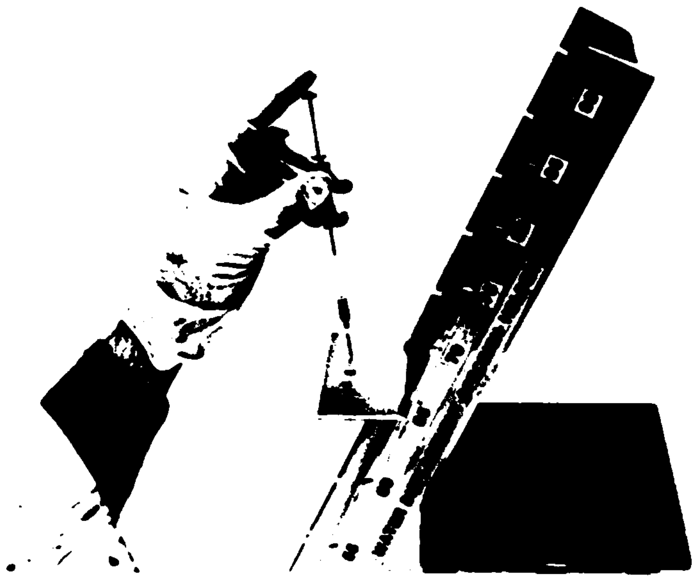


FIGURE 2. WATER DISPLACEMENT TEST PROCEDURE - APPLICATION OF WATER DROPLETS

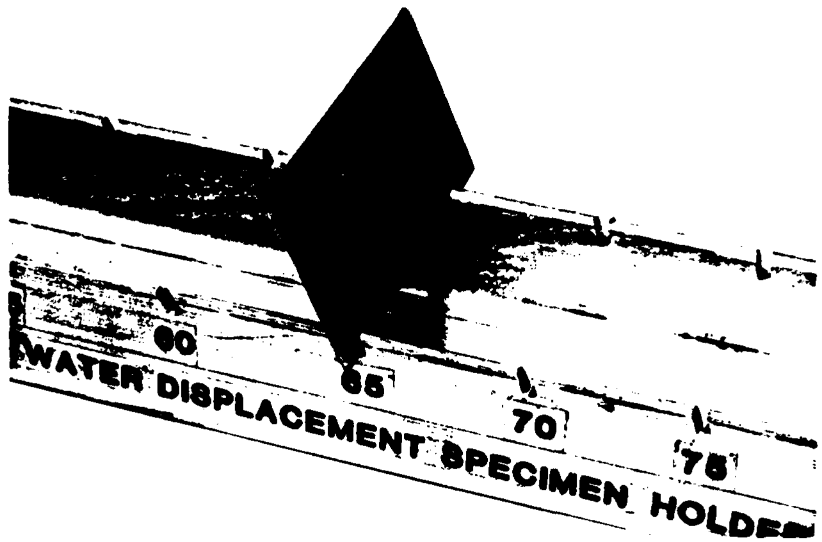


FIGURE 3. WATER DISPLACEMENT TEST PROCEDURE - SPECIMEN HOLDER LOWERED TO PLACE. SPECIMEN AT APPROPRIATE ANGLE (65°)

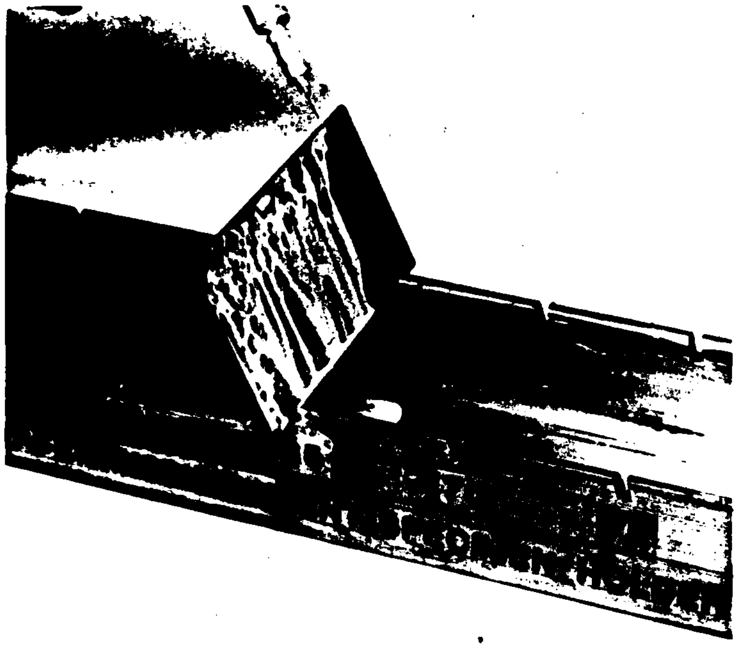


FIGURE 4. WATER DISPLACEMENT TEST PROCEDURE - TEST AGENT APPLIED TO UPPER EDGE OF SPECIMEN

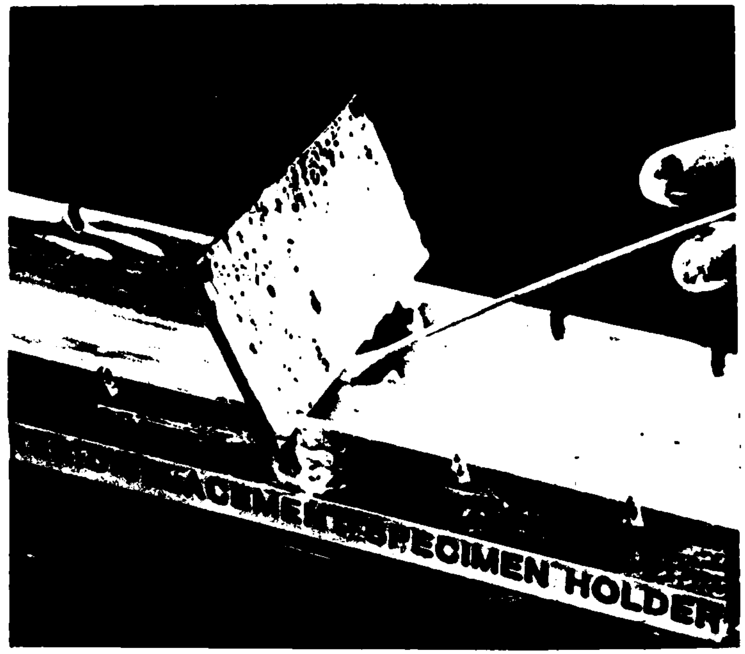


FIGURE 5. WATER DISPLACEMENT TEST PROCEDURE - ABSORB DISPLACED WATER USING COTTON SWAB

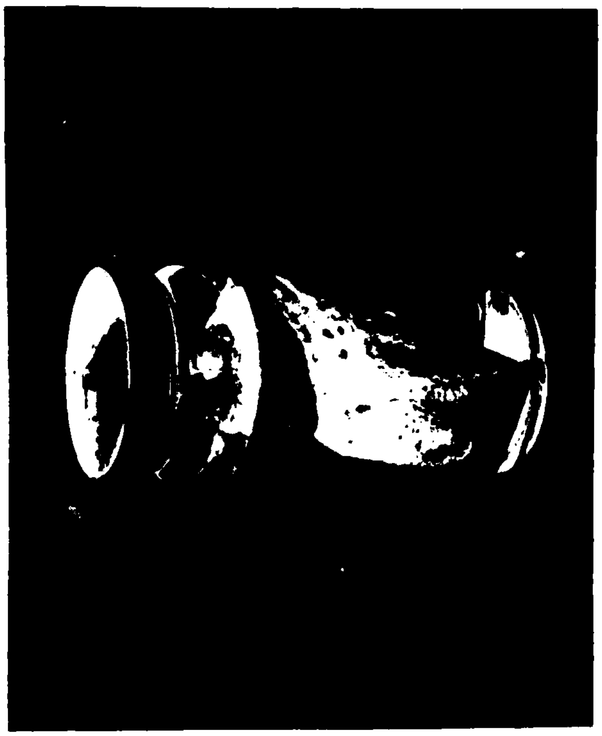


FIGURE 6. WATER DISPLACEMENT TEST PROCEDURE - SPECIMEN IMMERSED IN METHANOL IN AN AIR-TIGHT CONTAINER

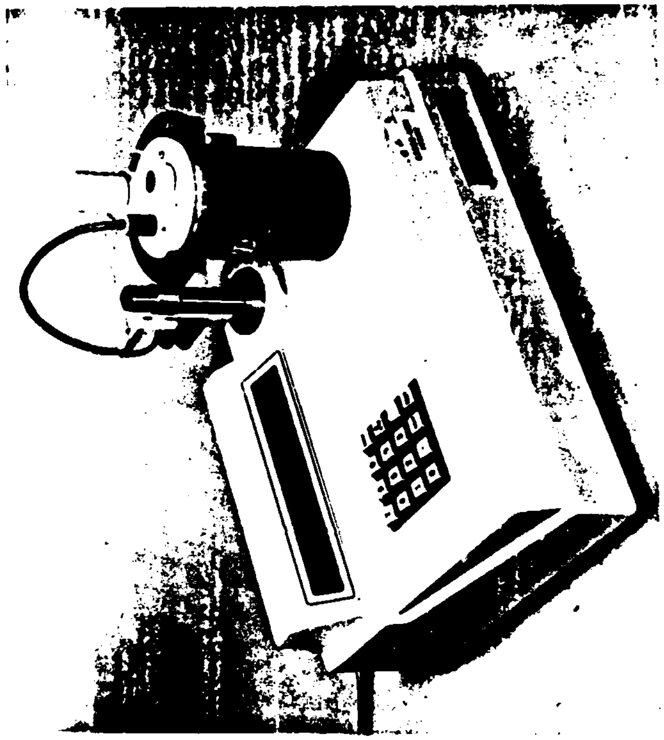


FIGURE 7. WATER DISPLACEMENT TEST PROCEDURE - METHANOL TITRATED FOR WATER CONTENT USING A KARL-FISHER AQUAMETER

The specimen was immersed for 24 hours to allow any water remaining on the specimen to be dissolved by the methanol. Preliminary studies indicate residual water on the specimen will be dissolved by the methanol within 24 hours.

The methanol was then tested for water content using a Karl-Fisher titration method (ASTM D-890), reference (q), Figure 6. This is a standard method for determining the water content of organic compounds. It is a coulometric titration which is dependent upon the reaction of water with pyridine. The specific chemical reactions and mechanisms used to determine water content by this method are presented in Appendix B. The results of the titration are recorded in milligrams of water remaining on a specimen.

Six replicates were tested at each angle for all agents. Four 1 ml methanol samples were extracted and titrated for each replicate. These four titrations were averaged to obtain $\bar{x}_i$, the water content of the methanol following agent application, for replicates (i) 1 through 6. The $\bar{x}_i$'s were then averaged to obtain $X_{(n,\theta)}$, the mean water content of the methanol following application of agent n at specimen angle θ. A standard deviation, s, of $X_{(n,\theta)}$ was also calculated.

The water content of the methanol at the time of titration is attributed to several factors:

1. The initial water content of the methanol, X_i.
2. Water sorbed on the steel specimen prior to the test.
3. Water present in the test agent prior to the test.
4. Water not displaced from the specimen after agent application.

Factors 1, 2, and 3 were accounted for by performing the following. Prior to testing the various agents for water displacement ability, the initial water content of the batch of methanol to be used was determined by the Karl-Fisher titration method. Also, controls of the blank specimen immersed in methanol and of specimens containing just the test agents were performed to determine the effect of the specimen and the agents on water content. Water remaining on the specimen following agent application, X_f, was then determined by:

$$X_f = X_{(n,\theta)} - X_i \qquad (2)$$

where: X_f = Water remaining on the specimen

$X_{(n,\theta)}$ = Water content of the methanol following agent application

X_i = Initial water cortent of the methanol

The results can also be expressed in terms of the percentage of water initially on a specimen which a test agent has displaced, water displacing efficiency (WDE). This is determined by equation (3):

$$WDE = \frac{W_i - W_f}{W_i} \times 100\% \qquad (3)$$

where: W_i = amount of water initially on a specimen prior to agent application (water sorbed on the steel specimen plus water introduced onto the specimen).

W_f = amount of water remaining on the specimen after agent application.

R E S U L T S

The detailed data obtained from the water displacement tests are listed in Appendix C. These results are summarized in Tables V, VI, and VII, and illustrated on Figures 8 through 14.

CONTROL DATA

Table V lists the water content of the titrated methanol contributed solely by a steel specimen and the test agents, the controls. From this data, it was concluded that the steel specimen contributed 21.3 milligrams of water to the methanol but that the test agents made no significant contribution to water content. The control line of Figure 8 through 12, "Water on a Specimen Prior to Agent Application," W_i, is the summation of the water contributed by the steel specimen, 21.3 milligrams, and the water introduced onto the specimen, 150.0 milligrams. W_i is equal to 171.3 milligrams of water.

TEST AGENT DATA

The test agent displacement data are presented on Tables VI and VII, and Figures 8 through 12. The 95 percent confidence interval illustrated on these figures was determined by reference (r):

$$X_{(n,\theta)} \pm 2.571\ (s/\sqrt{N})$$

where s is the standard deviation at point $X_{(n,\theta)}$, 2.571 is the Student's T distribution value for 95 percent confidence with five degrees of freedom, and N is equal to the number of replicates, 6.

The test results prove that the five test agents all vary in water displacing ability. Figure 8 illustrates SA-1 displaces water effectively, confirming previous studies, references (k) and (o). Water displacement is constant over the entire interval of specimen angles from 5 to 85 degrees with an average of 25.5 milligrams of water remaining on a specimen, a water displacing efficiency (WDE) of 85.1 percent.

Table V. Water Contribution by the Specimen and Test Agents - Controls (no water droplets added).

Control	Mean Water Content Contributed by Controls (milligrams of water)*	Standard Deviation (milligrams)
Blank Specimen	21.3	5.6
SA-1 on specimen	14.4	3.2
SA-2 on specimen	22.3	3.4
AC-1 on specimen	23.7	2.7
EE-1 on specimen	24.0	4.9
SA-3 on specimen	24.5	2.3

*Based on six replicates.

Table VI. Water Displacement Test Results
(171.3 milligrams of water on a specimen prior to agent application).

Angle, θ (degrees)	SA – 1		SA – 2		AC – 11		EE – 1		AC – 3	
	X_f	s	X_f	s	X_f	s	X_f	s	X_f	s
	(milligrams of water)									
5	25.9	11.7	47.6	13.4	137.2	12.3	159.4	1.2	161.7	8.8
10	24.7	4.9	18.8	18.8	86.4	8.2	159.8	3.3	144.6	14.6
15	24.1	4.4	23.5	8.6	84.0	17.1	110.5	15.3	52.9	12.4
20	30.9	5.2	23.3	9.5	80.3	3.4	39.5	11.6	15.1	4.2
25	27.1	3.3	27.6	9.5	79.4	14.3	50.9	11.0	15.7	5.2
30	26.3	4.2	31.4	9.4	80.5	6.8	45.8	4.3	19.6	6.1
35	25.4	7.9	24.2	5.6	81.1	9.8	46.8	3.2	23.0	6.4
40	22.8	5.6	27.6	7.2	43.2	1.3	42.9	1.9	25.4	6.1
45	22.1	5.7	28.6	6.4	19.3	3.2	37.8	4.7	24.3	4.4
50	28.4	4.4	28.3	7.4	17.5	2.7	38.5	5.3	28.3	6.2
55	26.4	6.1	23.3	3.6	28.4	6.5	45.2	4.6	27.6	5.0
60	22.9	4.2	26.5	5.3	20.7	4.9	48.6	4.4	29.4	5.6
65	24.5	4.7	25.4	5.5	23.7	5.8	46.9	4.4	25.7	3.7
70	24.7	4.0	25.2	4.9	24.2	4.9	44.7	5.3	27.9	4.6
75	25.5	5.0	27.3	5.3	23.0	6.7	44.7	5.8	27.1	3.5
80	24.8	4.4	24.2	4.7	24.8	20.1	46.3	4.8	23.3	4.1
85	27.9	4.5	26.7	4.2	30.5	22.3	46.9	4.6	24.2	2.4

* Based on six replicates.

Table VII. Test Results in Water Displacement Efficiency

Specimen Angle	SA-1	SA-2	AC-1	EE-1	SA-3
5	84.9	72.2	19.9	6.9	5.6
10	85.6	89.0	49.6	6.7	15.6
15	85.9	86.3	51.0	35.5	69.1
20	82.0	86.4	53.1	76.9	91.2
25	84.2	83.9	53.6	70.3	90.8
30	84.6	81.7	53.0	73.3	88.6
35	85.2	85.9	52.7	72.7	86.6
40	86.7	83.9	74.8	75.0	84.6
45	87.1	83.3	88.7	77.9	85.8
50	83.4	83.5	89.8	77.5	83.5
55	84.6	86.4	83.4	73.6	83.9
60	86.6	84.5	87.9	71.6	82.8
65	85.7	85.2	86.2	72.6	85.0
70	85.6	86.3	85.9	73.9	83.7
75	85.1	84.1	86.6	73.9	83.6
80	85.5	85.9	85.5	73.0	86.4
85	83.7	84.6	82.2	72.6	85.9

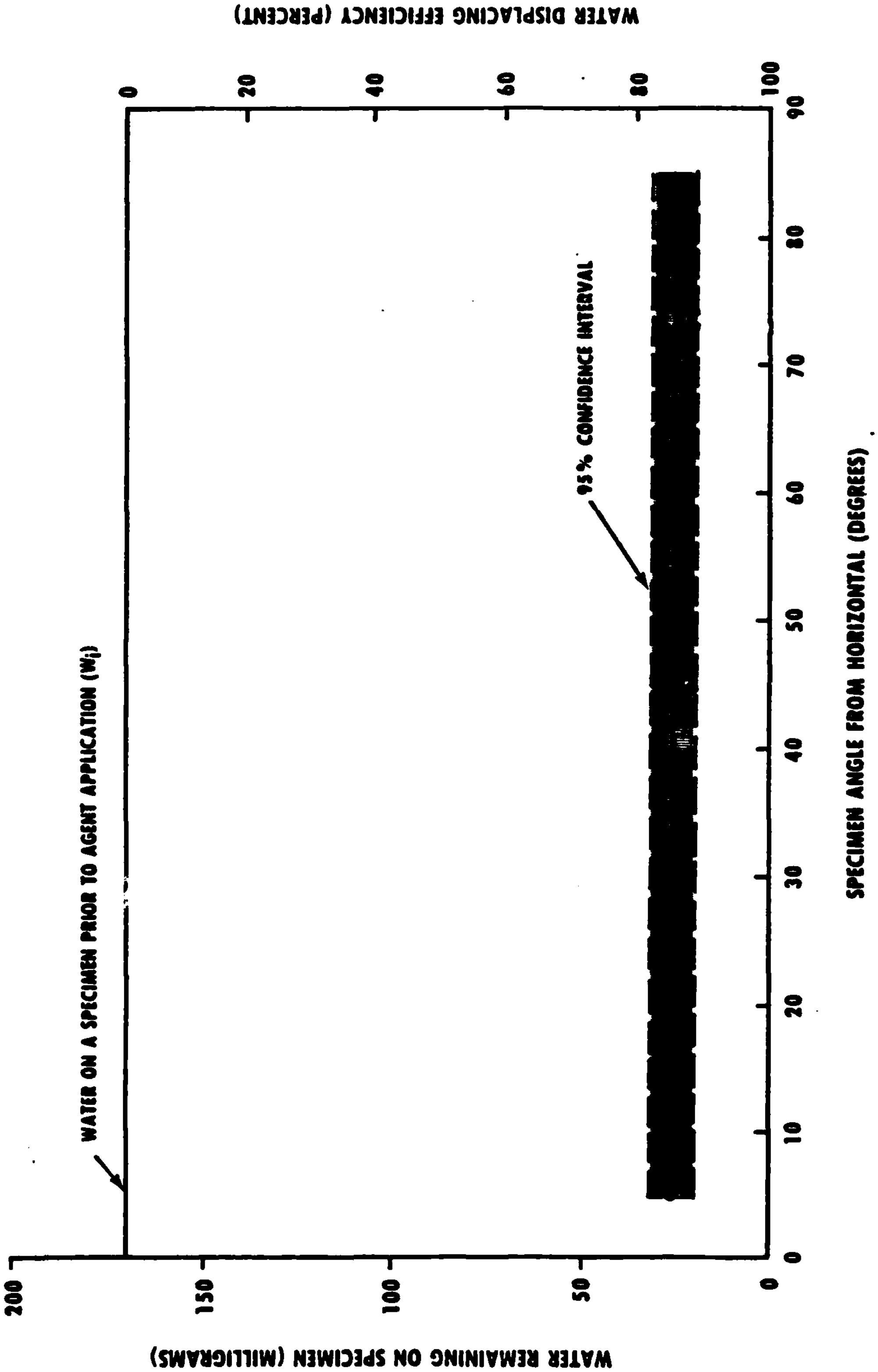


FIGURE 8. WATER DISPLACEMENT TEST RESULTS FOR SA-1.

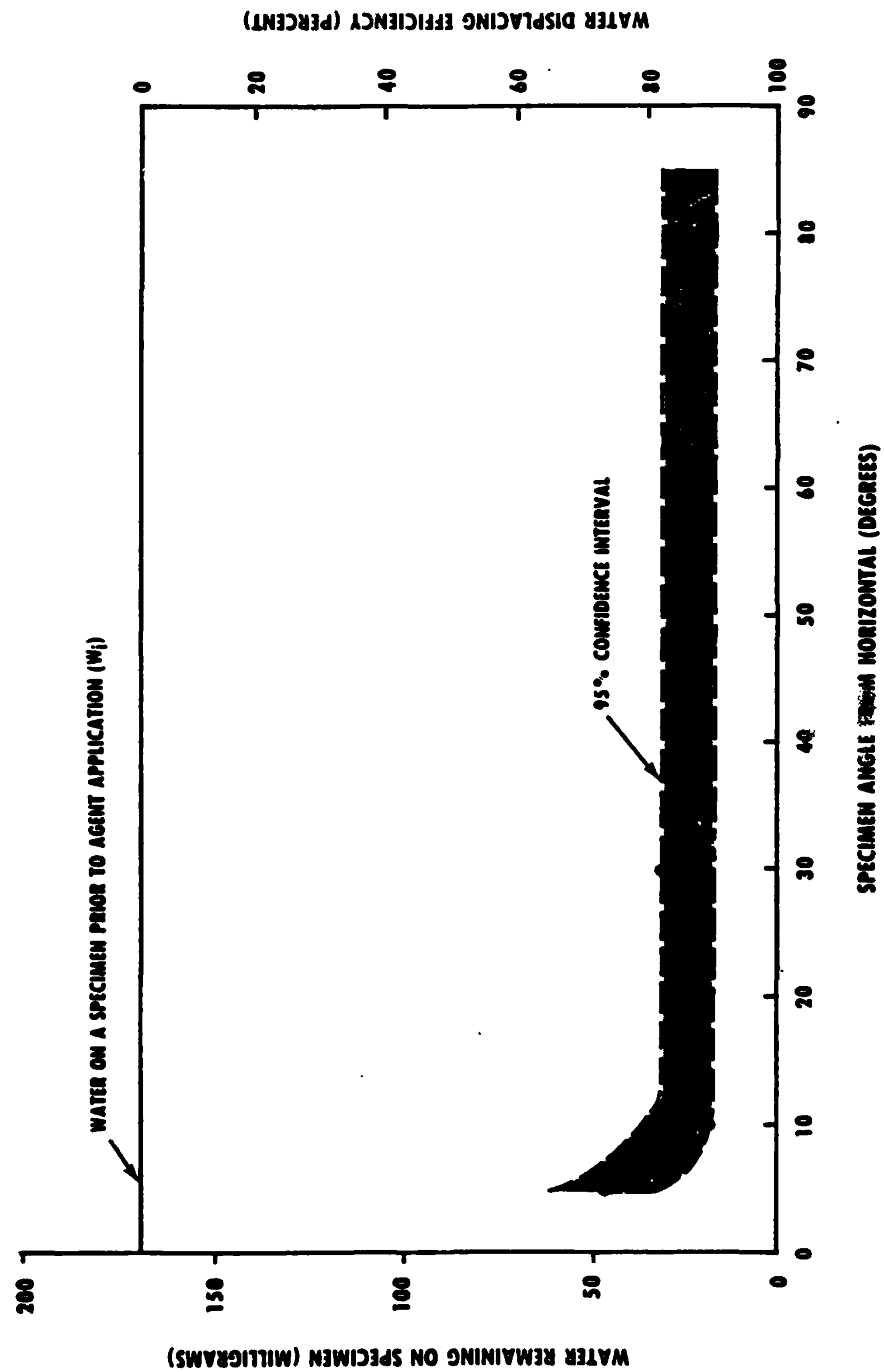


FIGURE 9. WATER DISPLACEMENT TEST RESULTS FOR SA-2.

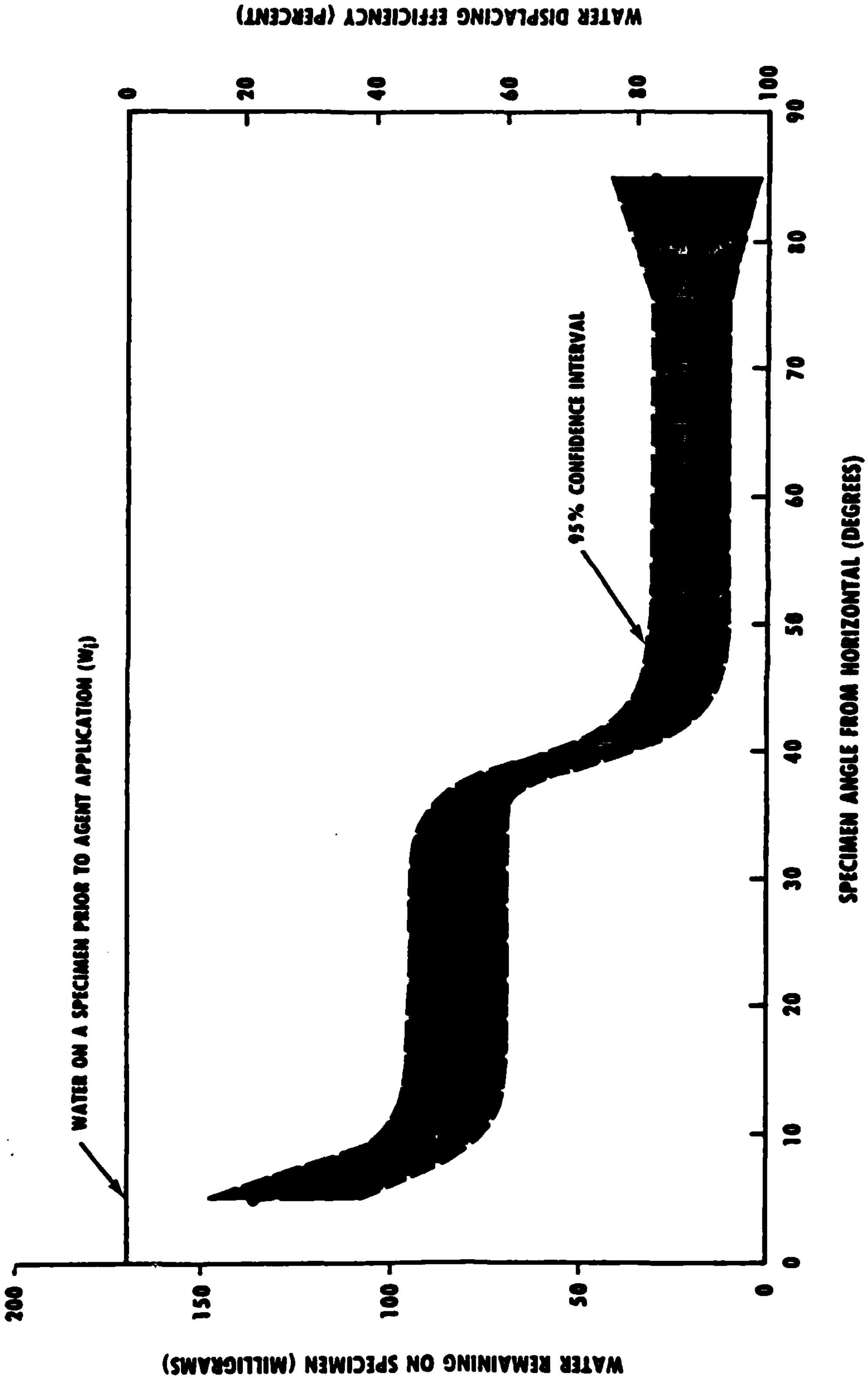


FIGURE 10. WATER DISPLACEMENT TEST RESULTS FOR AC-1.

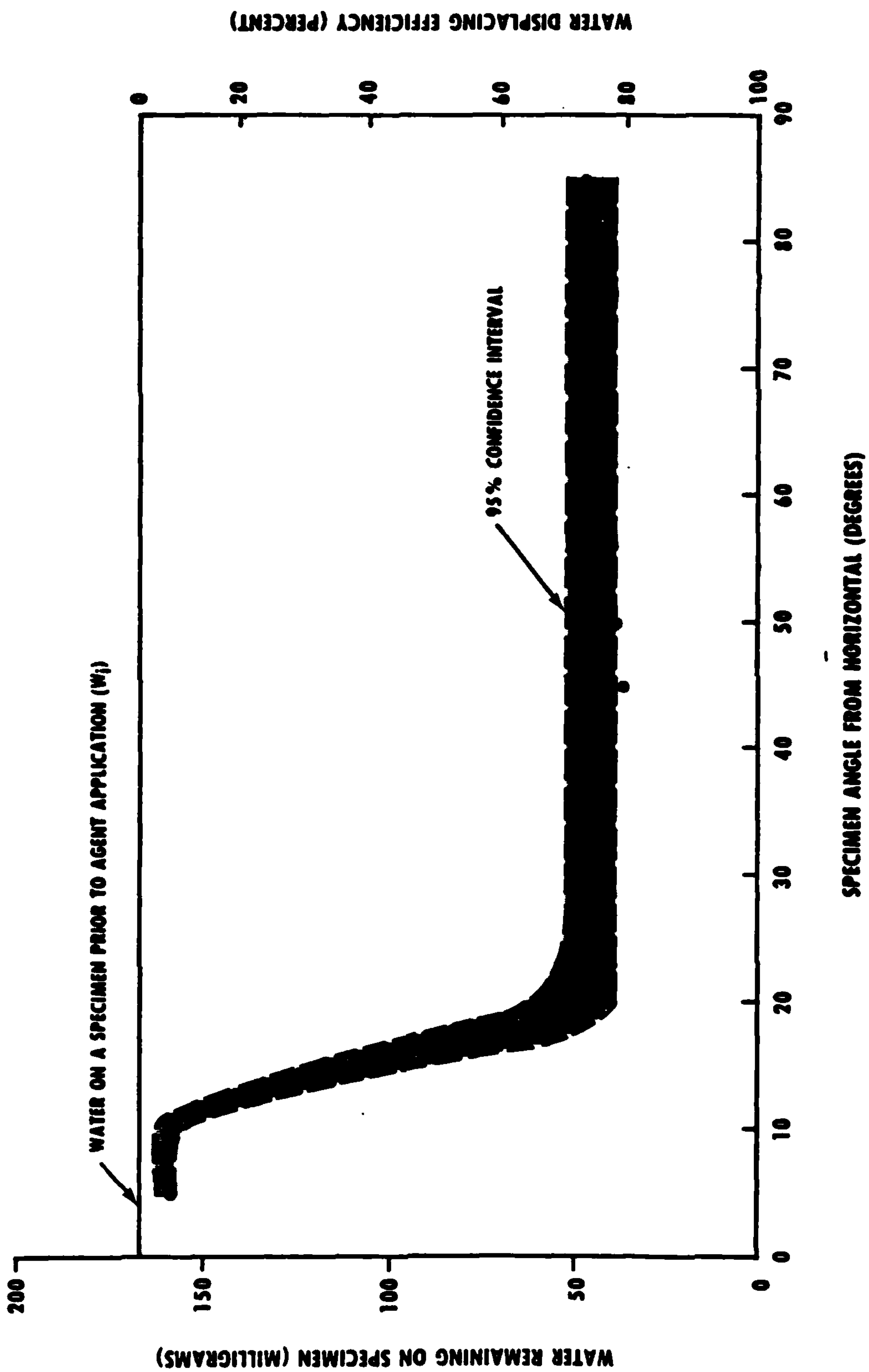


FIGURE 11. WATER DISPLACEMENT TEST RESULTS FOR EE-1.

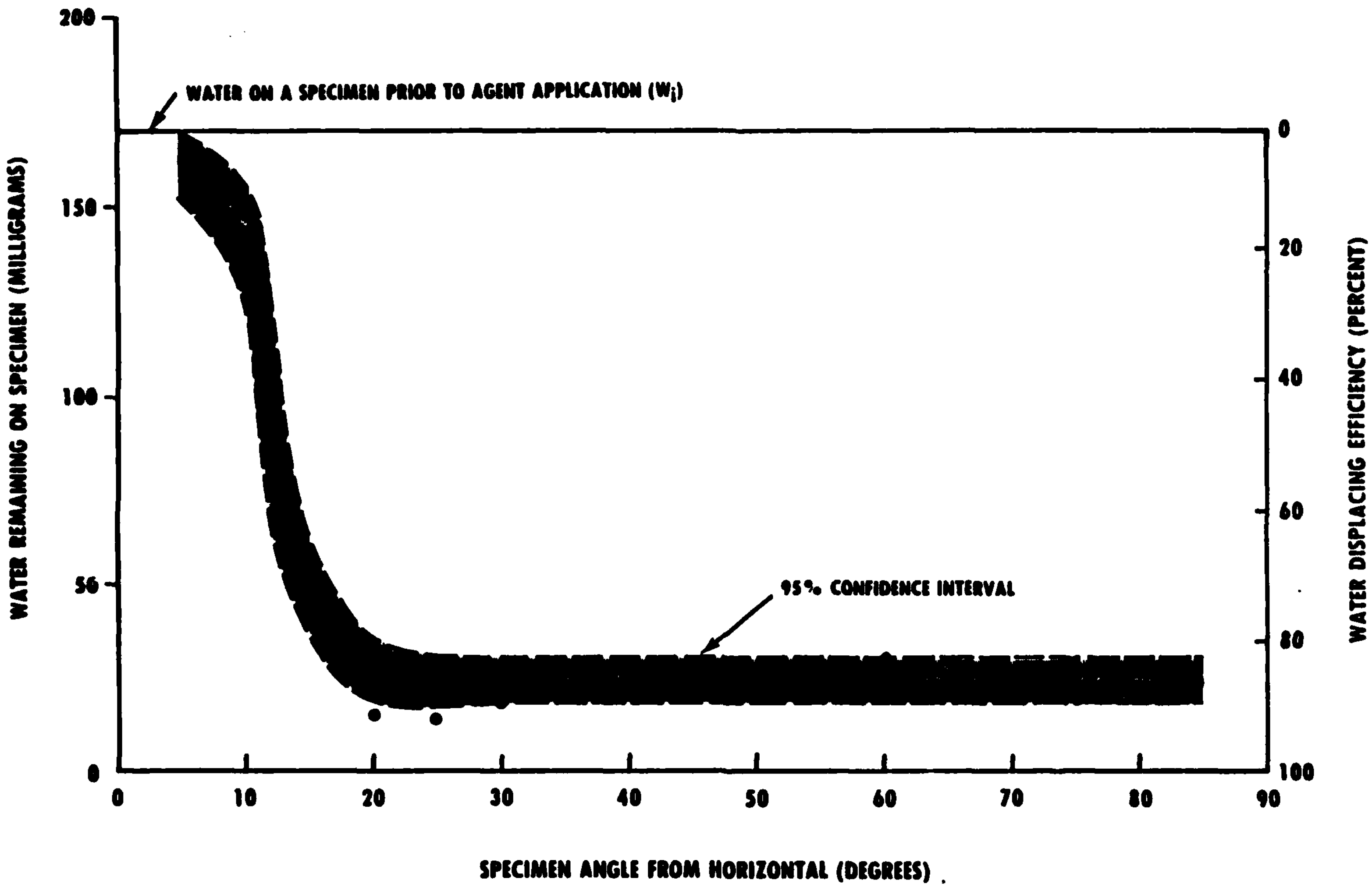


FIGURE 12. WATER DISPLACEMENT TEST RESULTS FOR SA-3.

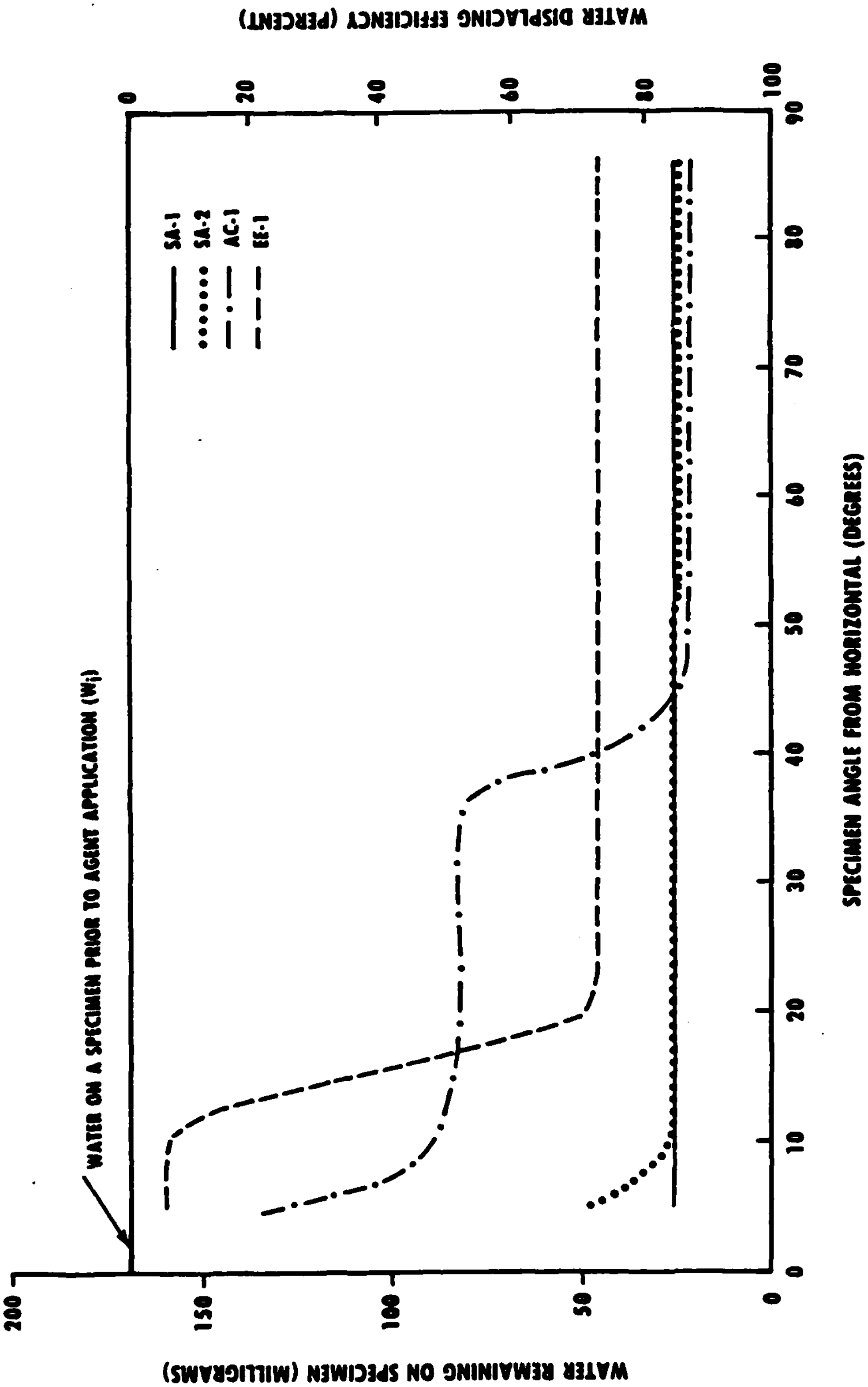


FIGURE 13. COMPARISON OF SA-1, SA-2, AC-1, and EE-1 - WATER DISPLACEMENT EFFICIENCY.

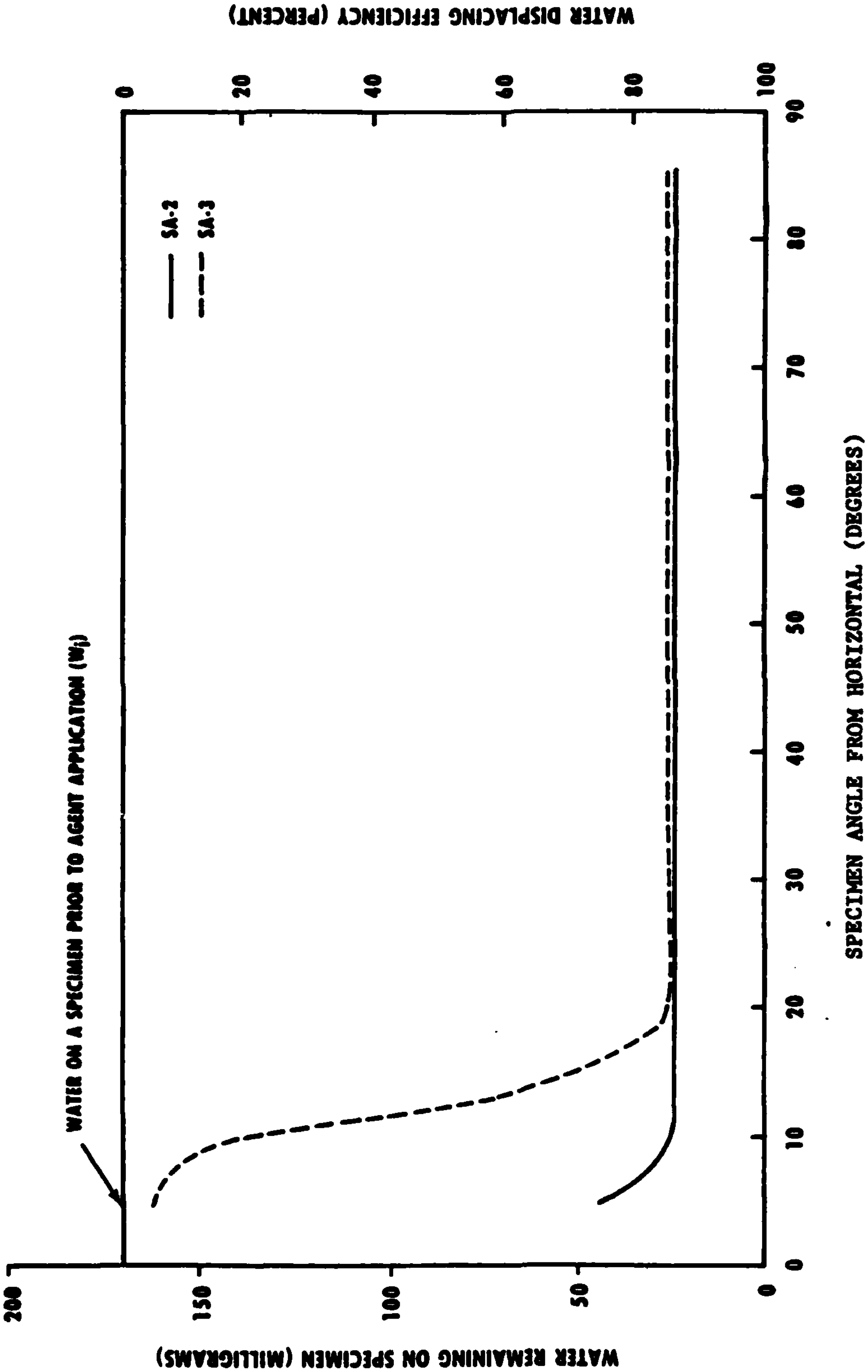


FIGURE 14. COMPARISON OF SA-2 AND SA-3 - WATER DISPLACEMENT EFFICIENCY.

The results for SA-2 also confirm previous studies, references (k) and (p) that proved this compound to be a good water displacer. Figure 9 suggests that SA-2 is only a fair water displacer at an angle of five degrees, with 47.6 milligrams of water remaining on the specimen, a WDE of 72.2 percent. Between 10 and 85 degrees, however, SA-2 is a good water displacer. Along this interval, the graph on Figure 4 is constant with an average of 25.9 milligrams of water remaining on the specimen, a WDE of 84.9 percent.

Figure 10 shows that AC-1 is a poor water displacer at angles less than 45 degrees but a good displacer at higher angles. At five degrees, 137.2 milligrams of water remain on the specimen and the WDE is 19.9 percent. Between 5 and 10 degrees, the WDE is increased to 52.1 percent where it remains constant to 35 degrees. From 35 to 45 degrees the WDE undergoes a transition up to 86.2 percent where it remains constant for angles from 45 to 85 degrees.

EE-1 is a poor water displacer. At 5 and 10 degrees, the WDE is approximately 6.8 percent. Between 10 and 20 degrees there is a transition in WDE up to 74 percent where it remains constant to 85 degrees. This is illustrated in Figure 11.

SA-3 is a poor water displacer at angles less than 20 degrees. At angles from 20 to 85 degrees, SA-3 is a good displacer with a WDE of 86 percent. This is illustrated in Figure 12.

Figure 13 compares SA-1, SA-2, AC-1, and EE-1. As previously mentioned, SA-1 and SA-2 are good water displacers while AC-1 and EE-1 are poor water displacers. This graph illustrates the difference in water displacing ability of the four compounds.

Figure 14 compares the water displacing ability of SA-2 and SA-3. SA-2 is similar in compositon to SA-3 except for the addition of petroleum sulfonate to SA-2 (See appendix B for compositions). This comparison was performed to examine the effect of sulfonates on water displacement. The graph clearly illustrates a difference in WDE at angles below 20 degrees where SA-2 is significantly more effective than SA-3. This confirms that sulfonates do assist in water displacement. This effect will be discussed later in this report.

DISPLACEMENT ACTION

During the test, as the test agents were flowing down the specimen, it was observed that when an agent contacted a drop, the contact angle of the water droplet rapidly decreased from approximately 85 degrees to less than 45 degrees. A similar effect has been previously reported, reference (k). Figure 15 is a series of photographs of a water drop on a horizontal steel specimen. The water drop is seen as a quarter of an ellipse on the left side of each photograph. A water displacing compound, AML-350 (see Appendix C for composition), was placed on the specimen (right of the droplet in the photographs) and allowed to flow into the droplet. The photographs were taken at intervals of 2.5 milliseconds. AML-350 contacts the drop at approximately frame 16. The action is completed by frame 27, after approximately 28 milliseconds. A similar action was observed when substituting SA-1 and SA-2 for AML-350.

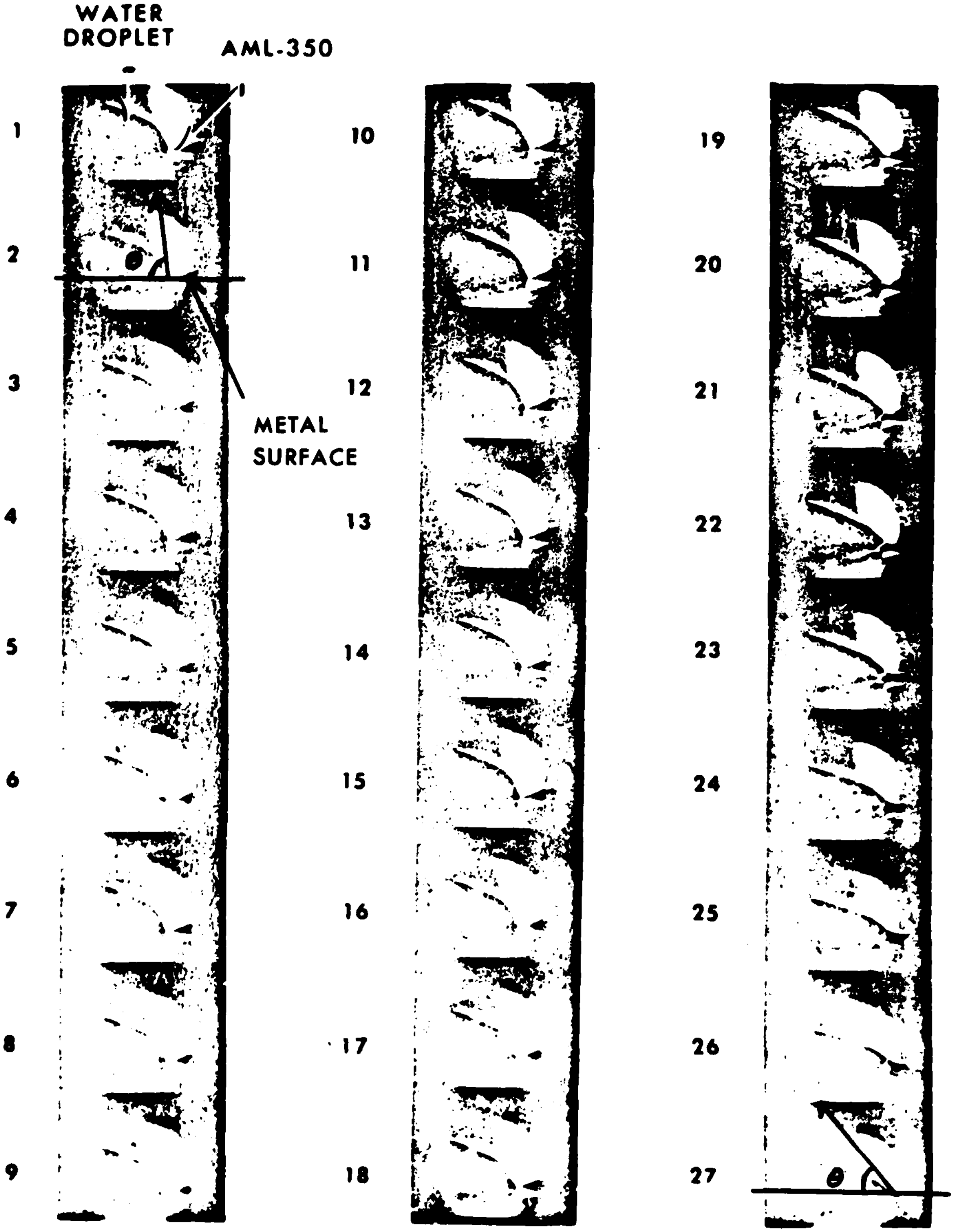


FIGURE 15. COLLAPSE OF WATER DROPLET LEADING EDGE UNDER 50X MAGNIFICATION REFERENCE (K)

DISCUSSION

The prime objective of this effort has been to devise and validate a quantitative test for the displacement of a discontinuous phase of water on a steel surface. The test method which has been presented has yielded results which agree with previous investigations, references (k), (o), and (p), and preliminary studies using the water drop test, reference (o). SA-1 and SA-2 have been confirmed to be good water displacers while the displacing ability of AC-1, EE-1, and SA-3 is dependent upon substrate angle and as such, these compounds are considered to be poor water displacers.

Unlike previous test methods, the current method yields data which is quantitative, providing a more precise means of evaluating compounds and allowing a better understanding of their displacing ability.

A secondary objective of this effort was to use the test results to discuss the proposed mechanism for displacing a discontinuous water phase. As previously described, the mechanism requires the displacing agent to:

1. Spread over the metal surface upon application, wetting the substrate.

2. Be immiscible with water to ensure no water entrapment in the displacing agent.

3. Have a higher affinity for the substrate than water in order for the agent to diffuse under the droplets and thus displace them from the surface.

While the test results did not validate the proposed mechanism, they support the interpretation of the displacing action.

The first requirement of water displacement is the ability of the agent to wet or spread over the substrate. Wettability is a thermodynamic property dependent upon the surface tension of the agent, the surface energy of the substrate, and the surface energy of the interface between these two phases. The agents tested were formulated specifically to be surface coatings and as such they were designed to wet steel substrates. It can be deduced however, that if the agents did not wet and spread over the substrate, they would not contact the water droplets and could not displace them. Therefore, wettability is required for displacement to occur.

The second requirement for water displacement is agent - water immiscibility. All of the test agents are virtually immiscible with water. If an agent was miscible, however, mixing could ensue after agent application, entrapping water. This water would be unable to be displaced by the agent and would remain on the specimen, resulting in a lower water displacing efficiency.

The third requirement of the proposed mechanism is that the agent have a high affinity for the substrate. This is accomplished by a large adsorption driving force of the agent onto the solid surface. Agent adsorption was

designed as a factor in this study by addition of petroleum sulfonate to a test agent. SA-2 is similar in composition to SA-3 except for the addition of petroleum sulfonate to SA-2 (see Appendix A for compositions).

Petroleum sulfonates have heats of adsorpotion on steel of approximately 10 kilocalories per mole, reference (s). This is high relative to most compounds. For example, alcohols have been found to have heats of adsorption ranging from 3.7 kcals per mole for methanol to 4.8 kcals per mole for octadecanol, with the heat of adsorption increasing with molecular weight, reference (t). Fatty acids have been found to have heats of adsorption on steel ranging from 2.1 kcals per mole for acetic acid to 5.3 kcals per mole for stearic acid, also increasing with molecular weight, reference (t). Castor oil, which contains an ester group, has a heat of adsorption onto steel of 2.3 kcals per mole, reference (u).

Figure 9 compares the water displacement abilities of SA-2 and SA-3. The graph clearly illustrates a difference in water displacing efficiency at angles less than 20 degrees where SA-2 is significantly more effective than SA-3. At angles above 20 degrees, the water displacing ability of the two compounds is comparable. With the only difference between SA-2 and SA-3 being the sulfonate addition to SA-2, the test results suggest that the high affinity requirement of the proposed mechanism is accurate; compounds with high affinities for the solid surface will perform better than those with less affinity for the surface.

An observation was made while studying the displacing efficiencies of all the test agents. The test results illustrate poor water displacers are not effective at low specimen angles. As the angle of inclination increases, these agents become effective water displacers. Good water displacers perform well at all angles. With these observations and the proposal of adsorption assisting in water displacement, one can infer that the graphs illustrate two effects occurring during the test, an adsorption effect and a gravity effect.

The adsorption effect is observed at low angles with the efficient water displacers. The agent preferentially adsorbs onto the solid surface, then diffuses between the water phase and the solid phase. At this point, the contact angle of the water droplet rapidly decreases and the water spreads over the displacing agent, eventually flowing off of the specimen. This is not observed with poor water displacers which will not adsorb as strongly and cannot diffuse under the droplets. Although this adsorption effect is best observed at low angles, it is not dependent upon angle.

The gravity effect is observed at higher angles with the poor water displacers. The agent will flow down the specimen and contact a water drop. The impact, in conjunction with the force of gravity and the high specimen angle, will cause the water drop to flow down and off of the specimen. Although this is best observed with poor water displacers, gravity obviously assists all compounds in their ability to displace water. The gravity effect is dependent upon angle in that the force of gravity affecting the water drops' ability to remain on the specimen is controlled by the trigonometric sine of the specimen angle.

In summary, the water displacement test will quantitatively differentiate the ability of compounds to displace water. The data obtained may also be used to discuss existing theories and assist in further investigation of water displacement.

CONCLUSIONS

A water displacement test method has been devised. The method includes the application of water droplets onto a steel surface, followed by the application of a test agent. The specimen is immersed in methanol which absorbs residual water on the specimen. The methanol is then analyzed for water content, yielding a quantitative result for water displacement.

The method can be used to compare the water displacing efficiency of compounds. It can also be used to further investigate the phenomenon of water displacement.

Water displacement at low angles is controlled by preferential adsorption of the test agent onto the substrate. At high angles, water displacement is controlled by the force of gravity acting on the water drop after the agent makes contact with the drop. The displacing action has been observed to occur within several milliseconds.

Petroleum sulfonates assist in the displacement of water by strongly adsorbing onto the surface, allowing the agent to diffuse between the water drop and the solid surface.

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APPENDIX A

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APPENDIX A

COMPOSITION OF SA-1(a)

	PERCENT (WEIGHT)
Isopropanol	4.6
Aromatic Hydrocarbon (b)	21.2
Trichlorotrifluoroethane	28.6
Ethyl Cellulose (c)	0.4
Barium Sulfonate (d)	4.0
Alkyl Ammonium Organic Phosphate (e)	1.0
Silicone Varnish (f)	5.1
Silicone Resin (g)	5.1
Silicone Alkyd Resin (h)	30.0
	100.0

(a) This material is marketed commercially as AMLGUARD. It conforms with Military Specification Mil-C-85054.

(b) Amsco Solvent G (American Mineral Spirits Co.)

(c) T-200 (Hercules Powder)

(d) NaSul BSN (R.T. Vanderbilt Co.)

(e) R.P. No. 2 (E. I. DuPont)

(f) DF-88 (General Electric)

(g) SR-82 (General Electric)

(h) Varkyd 385-50R (McCloskey Varnish Co.)

COMPOSITION OF SA-2

	PERCENT (WEIGHT)
Silicone Alkyd Resin (a)	39.1
Ethyl Acetate	19.4
Mineral Spirits (b)	11.7
1,1.1 Trichlorotrifluoroethane	7.7
Sodium Petroleum Sulfonate (c)	2.1
Rutile; titanium Dioxide (d)	11.5
Zinc Molybdate (e)	6.4
Isopropyl, Tri(N-ethylamino-ethylamino) titanate (f) (4.5% in isopropyl alcohol)	2.1
	100.0

(a) Varkyd 385-50E (McCloskey Varnish Co.)

(b) AMSCO Solvent G (Union Oil of California)

(c) Alox 904 (Alox Corporation)

(d) R-960 (E. I. DuPont)

(e) Moly-White 101 (Sherwin Williams Chemicals)

(f) KR-44S (Kenrich Chemicals)

COMPOSITION OF AC-1 (a)

	PERCENT (WEIGHT)
Acrylic Resin (b)	43.6
Acrylic Resin (c)	32.8
Titanium Dioxide	18.4
Cellosolve Acetate	3.8
Plasticizer (d)	1.4
	100.0

(a) This material conforms with Military Specification Mil-C-81352.

(b) Acryloid A-21 (Rohm and Haas Co.)

(c) Acryloid B-44 (Rohm and Haas Co.)

(d) Santicizer 160 (Monsanto Co.)

COMPOSITION OF EE-1

	PERCENT (WEIGHT)
Epoxy Ester Resin (a)	80.0
Xylene	20.0
	100.0

(a) Varkyd 13-50x (McCloskey Varnish Company)

COMPOSITION OF SA-3

	PERCENT (WEIGHT)
Silicone Alkyd Resin (a)	39.9
Ethyl Acetate	19.8
Mineral Spirits (b)	11.9
1,1,1 Trichlorotrifluoroethane	7.9
Rutile; titanium dioxide (c)	11.7
Zinc Molybdate (d)	6.5
Isopropyl, Tri(N-ethylamino-ethylamino) Titanate (e) (4.5% in ethyl alcohol)	2.3
	100.0

(a) Varkyd 385-50E (McCloskey Varnish Company)

(b) AMSCO Solvent G (Union Oil of California)

(c) R-960 (E. I. DuPont)

(d) Moly-White 101 (Sherwin Williams Chemicals)

(e) KR-44S (Kenrich Chemicals)

COMPOSITION OF AML-350 (a)

	PERCENT (WEIGHT)
Barium Petroleum Sulfonate (b)	50.0
Mineral Spirits (c)	50.0
	100.0

(a) This material conforms with Military Specification Mil-C-81309, Type II.

(b) Alox 2028 (Alox Corporation)

(c) Mineral Spirits conforming with Federal Specification TT-T-291.

APPENDIX B

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APPENDIX B

KARL-FISHER METHOD OF DETERMINING WATER CONTENT OF METHANOL

The test was performed using an Aquatest IV Aquameter manufactured by Photovolt Corporation. The principles of determining water content are as follows. The methanol is titrated with a Karl-Fisher reagent which is a mixture of iodine, sulfur dioxide, pyridine, and methanol. The reagent reacts with water as follows:

$$C_5H_5N\cdot I_2 + C_5H_5N\cdot SO_2 + C_5H_5N + H_2O \rightarrow$$

$$2C_2H_5N{<}^{H}_{I} + C_5H_5N{<}^{SO_2}_{O} \quad \text{and} \quad C_5H_5N{<}^{SO_2}_{O} + CH_3OH \rightarrow$$

$$C_5H_5N{<}^{H}_{SO_3CH_3}$$

When water is present, the electrodes of the aquameter which are in the solution remain polarized. As water reacts with the reagent during titration, the electrodes become depolarized. Finally, a slight excess of iodine will totally depolarize the electrodes, allowing a large increase in current flow through a micrometer. When the micrometer records a current of 40 microamps for 30 seconds, the titration is complete. The amount of water initially present is caluclated by:

$$\frac{(\text{ml of KF reagent used}) \times (\text{mg } H_2O/\text{ml KF reagent}) \times (1000\ \text{g/mg})}{(\text{ml of sample titrated}) \times (\text{SpG of methanol})}$$

= micrograms of water per gram of methanol

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APPENDIX C

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APPENDIX C

TEST AGENT: CONTROLS

Control	Titration	x_1	x_2	x_3	x_4	x_5	x_6	$X_{n,\theta}$	X_i	X_f
	(milligrams of water)									
Steel Specimen	1	316	308	298	306	313	308		287	
	2	307	323	312	302	316	311		290	
	3	329	327	314	306	314	307		299	
	4	326	317	302	312	317	308		292	
	$\bar{x}_i$	317.3	318.8	306.5	306.5	315.0	308.5	312.1	290.8	21.3
	S^i							5.6	7.0	
SA-1 on Steel Specimen	1	300	310	303	298	302	308			
	2	317	310	307	304	305	303			
	3	314	307	303	300	300	305			
	4	304	309	305	300	307	304			
	$\bar{x}_i$	308.7	309.0	304.5	300.5	303.5	305.0	305.2	290.8	14.4
	S^i							3.2	7.0	
SA-2 on Steel Specimen	1	92	92	97	90	101	96		71	
	2	92	103	98	95	96	97		70	
	3	95	105	105	98	98	99		81	
	4	102	109	110	96	98	95		82	
	$\bar{x}_i$	95.3	102.3	102.5	94.8	98.3	96.8	98.3	76.0	22.3
	S^i							3.4	6.4	
AC-1 on Steel Specimen	1	99	92	91	102	105	97			
	2	101	98	100	99	104	99			
	3	105	102	99	100	99	99			
	4	107	102	95	95	103	98			
	$\bar{x}_i$	103.0	98.5	96.3	99.0	102.8	98.3	99.7	76.0	23.7
	S^i							2.7	6.4	
EE-1 on Steel Specimen	1	103	95	102	92	106	99			
	2	106	94	98	95	108	101			
	3	108	98	99	96	107	98			
	4	104	95	98	94	104	98			
	$\bar{x}_i$	105.3	95.5	99.2	94.3	106.3	99.0	100.0	76.0	24.0
	S^i							4.9	6.4	

TEST AGENT: CONTROLS

Control	Titration (milligrams of water)	x_1	x_2	x_3	x_4	x_5	x_6	$X_{n,o}$	X_i	X_f
SA-3 on Steel Specimen	1	62	57	57	64	63	59		38	
	2	60	59	57	64	63	61		37	
	3	63	59	61	66	65	62		35	
	4	64	60	59	63	61	62		37	
	$\overline{x}_i$	62.3	58.8	58.5	64.3	63.0	61.0	61.3	36.8	24.5
	S^i							2.3	1.9	

TEST AGENT: SA-1

Angle	Titration	x_1	x_2	x_3	x_4	x_5	x_6	$X_{n,\Theta}$	X_i	X_f
	(milligrams of water)									
5	1	77	78	83	105	83	88		57	
	2	72	81	86	112	85	87		60	
	3	82	77	86	110	74	86		65	
	4	82	82	84	111	80	88		61	
	$\overline{x}_i$	78.3	79.5	84.8	109.5	80.4	87.3	86.7	60.8	25.9
	S^i							11.7	3.3	
10	1	89	85	79	84	80	86			
	2	91	83	84	89	79	84			
	3	95	77	86	92	81	89			
	4	92	80	84	87	80	85			
	$\overline{x}_i$	91.8	81.3	83.3	90.5	80.0	86.1	85.5	60.8	24.7
	S^i							4.9	3.3	
15	1	74	82	70	73	74	70		46	
	2	75	79	71	72	77	70		51	
	3	77	80	69	74	75	69		51	
	4	76	82	67	75	76	67		51	
	$\overline{x}_i$	75.5	80.8	69.3	73.5	75.5	69.0	73.9	49.8	24.1
	S^i							4.4	2.5	
20	1	89	98	85	88	102	86		59	
	2	91	95	82	91	99	87		61	
	3	91	95	87	86	98	84		60	
	4	84	96	84	89	103	86		59	
	$\overline{x}_i$	88.8	96.0	84.5	88.5	100.5	85.8	90.7	59.8	30.9
	S^i							6.2	1.0	
25	1	82	86	90	91	84	92			
	2	84	88	88	93	87	87			
	3	80	84	88	90	84	88			
	4	82	83	89	91	86	87			
	$\overline{x}_i$	82.0	85.3	88.8	91.3	85.3	88.5	86.9	59.8	27.1
	S^i							3.3	1.0	

TEST AGENT: SA-1

Angle	Titration	x_1	x_2	x_3	x_4	x_5	x_6	$X_{n,\theta}$	Σ_i	X_f
	(milligrams of water)									
30	1	92	84	84	80	89	86			
	2	94	78	88	82	87	89			
	3	89	82	87	84	86	85			
	4	91	80	92	85	87	84			
	$\bar{x}_i$	91.5	81.0	87.8	82.8	87.3	86.0	86.1	59.8	26.3
	S^i							4.2	1.0	
35	1	102	105	113	105	95	95		78	
	2	104	111	116	111	94	98		81	
	3	102	110	112	113	91	93		80	
	4	109	112	114	106	96	98		77	
	$\bar{x}_i$	104.3	109.5	113.8	108.8	94.0	96.0	104.4	79.0	25.4
	S^i							7.9	1.8	
40	1	102	96	97	105	102	110			
	2	105	97	95	110	98	113			
	3	105	95	94	108	95	105			
	4	103	99	98	104	101	108			
	$\bar{x}_i$	103.8	96.0	96.0	107.0	99.0	109.0	101.8	79.0	22.8
	S^i							5.6	1.8	
45	1	104	98	102	92	112	103			
	2	106	92	103	98	109	103			
	3	105	91	100	99	111	97			
	4	109	95	96	97	105	99			
	$\bar{x}_i$	106.0	94.0	100.3	96.5	109.3	100.5	101.1	79.0	22.1
	S^i							5.7	1.8	
50	1	123	112	119	127	123	130		100	
	2	126	117	125	130	123	126		92	
	3	122	118	121	123	127	129		92	
	4	122	114	125	125	128	125		96	
	$\bar{x}_i$	123.3	115.3	122.5	125.3	125.3	127.5	123.4	95.0	28.4
	S^i							4.4	3.9	

TEST AGENT: SA-1

Angle	Titration	x_1	x_2	x_3	x_4	x_5	x_6	$X_{n,\theta}$	X_i	X_f
	(milligrams of water)									
55	1	123	133	116	112	119	128			
	2	119	134	121	115	121	119			
	3	124	129	121	116	122	129			
	4	111	130	119	111	117	123			
	$\overline{x}_i$	119.3	131.5	119.3	113.5	119.8	124.8	121.4	95.0	26.4
	S							6.1	3.9	
60	1	116	113	119	123	109	122			
	2	123	111	124	125	113	124			
	3	121	116	119	121	114	119			
	4	119	115	118	123	111	119			
	$\overline{x}_i$	119.8	113.8	120.0	123.0	111.8	121.0	117.9	95.0	22.9
	S							4.2	3.9	
65	1	100	103	110	104	95	98		79	
	2	94	107	108	99	98	101		73	
	3	96	105	105	101	99	96		76	
	4	98	105	109	98	94	97		77	
	$\overline{x}_i$	97.0	105.0	108.0	100.5	96.5	98.0	100.8	75.3	24.5
	S							4.7	2.5	
70	1	95	107	105	105	102	98			
	2	99	111	102	96	98	96			
	3	94	108	103	98	103	101			
	4	96	105	100	98	103	101			
	$\overline{x}_i$	96.0	107.8	102.5	99.3	101.5	99.0	101.0	76.3	24.7
	S							4.0	2.5	
75	1	94	99	111	105	105	99			
	2	91	101	109	102	99	105			
	3	95	98	107	104	101	105			
	4	96	100	110	100	105	102			
	$\overline{x}_i$	94.0	99.5	109.3	102.8	102.5	102.8	101.8	76.3	25.5
	S							5.0	2.5	

TEST AGENT: SA-1

Angle	Titration	x_1	x_2	x_3	x_4	x_5	x_6	$X_{n,\theta}$	X_i	X_f
	(milligrams of water)									
80	1	109	103	96	105	96	96			
	2	111	106	98	102	99	101			
	3	105	105	99	100	98	99			
	4	107	101	95	101	98	96			
	$\bar{x}_i$	107.5	104.8	97.0	102.0	97.5	98.0	101.1	76.3	24.8
	S^i							4.4	2.5	
85	1	109	116	111	121	121	116		85	
	2	108	114	113	120	120	114		87	
	3	111	111	113	122	120	114		88	
	4	108	116	111	120	118	117		89	
	$\bar{x}_i$	109.0	114.3	112.0	120.8	119.8	115.3	115.2	87.3	27.9
	S^i							4.5	1.7	

TEST AGENT: SA-2

Angle	Titration	x_1	x_2	x_3	x_4	x_5	x_6	$X_{n,\theta}$	X_i	X_f
	(milligrams of water)									
5	1	87	79	114	103	83	95		49	
	2	90	84	116	97	77	91		42	
	3	95	85	119	100	82	89		50	
	4	96	80	118	95	81	98		46	
	$\bar{x}_i$	92.0	82.0	116.8	101.3	80.8	93.3	94.4	46.8	47.6
	S_i							13.4	3.6	
10	1	55	55	107	58	52	56			
	2	68	65	102	57	56	53			
	3	67	65	100	53	52	54			
	4	65	64	103	54	56	57			
	$\bar{x}_i$	63.8	62.3	103.0	55.5	54.0	55.0	65.6	46.8	18.8
	S_i							18.8	3.6	
15	1	65	57	70	70	86	62			
	2	70	63	71	75	84	64			
	3	71	60	74	74	87	66			
	4	68	59	70	77	81	63			
	$\bar{x}_i$	68.5	59.8	71.3	74.0	84.5	63.8	70.2	46.8	23.5
	S_i							8.6	3.6	
20	1	84	74	63	70	60	70			
	2	90	78	65	67	58	69			
	3	85	76	59	68	58	75			
	4	82	72	58	64	63	74			
	$\bar{x}_i$	85.3	75.0	61.3	67.3	59.8	72.0	70.1	46.8	23.3
	S_i							9.5	3.6	
25	1	84	58	63	56	70	67		38	
	2	84	60	61	58	74	67		45	
	3	86	63	69	61	69	65		35	
	4	83	59	63	63	68	63		39	
	$\bar{x}_i$	84.3	60.0	61.5	59.5	70.3	65.5	66.9	39.3	27.6
	S_i							9.5	4.2	

TEST AGENT: SA-2

Angle	Titration	x_1	x_2	x_3	x_4	x_5	x_6	$X_{n,\Theta}$	X_i	X_f
	(milligrams of water)									
30	1	60	82	67	83	65	63			
	2	64	79	70	86	63	63			
	3	63	84	66	80	62	67			
	4	59	82	74	82	64	68			
	$\overline{x}_i$	61.5	81.8	69.3	82.8	63.5	65.3	70.7	39.3	31.4
	S^i							9.4	4.2	
35	1	65	63	57	68	70	57			
	2	64	60	59	70	74	58			
	3	61	61	60	66	69	56			
	4	66	59	58	68	75	60			
	$\overline{x}_i$	64.0	60.8	58.5	68.0	72.0	57.8	63.5	39.3	24.2
	S^i							5.6	4.2	
40	1	59	69	65	78	70	60			
	2	63	74	63	75	67	57			
	3	61	68	61	80	68	63			
	4	58	68	64	82	72	60			
	$\overline{x}_i$	60.3	69.8	63.3	78.8	69.3	60.0	66.9	39.3	27.6
	S^i							7.2	4.2	
45	1	104	122	116	123	112	116		82	
	2	102	124	112	125	109	112		88	
	3	109	119	114	122	110	117		89	
	4	108	119	112	119	108	116		85	
	$\overline{x}_i$	105.8	121.0	113.5	122.3	109.8	115.3	114.6	86.0	28.6
	S^i							6.4	3.2	
50	1	126	115	105	103	109	121			
	2	121	118	105	101	116	119			
	3	124	112	110	105	115	123			
	4	123	113	114	109	112	124			
	$\overline{x}_i$	123.5	114.5	108.5	104.5	113.0	121.8	114.3	86.0	28.3
	S^i							7.4	3.2	

TEST AGENT: SA-2

Angle	Titration (milligrams of water)	x_1	x_2	x_3	x_4	x_5	x_6	$X_{n,\theta}$	X_i	X_f
55	1	105	109	114	105	119	108			
	2	104	112	113	104	110	105			
	3	102	105	108	110	116	108			
	4	106	112	111	113	114	110			
	$\bar{x}_i$	104.3	109.5	111.5	108.0	114.8	107.8	109.3	86.0	23.3
	S^i							3.6	3.2	
60	1	82	69	90	79	75	73		51	
	2	86	74	88	73	82	73		56	
	3	81	74	84	77	80	77		53	
	4	84	73	87	81	79	81		51	
	$\bar{x}_i$	83.3	72.5	87.3	77.5	79.0	76.0	79.3	52.8	26.5
	S^i							5.3	2.4	
65	1	83	76	86	84	69	77			
	2	76	73	84	79	67	80			
	3	78	72	85	85	74	81			
	4	79	74	87	80	71	75			
	$\bar{x}_i$	79.0	73.8	85.5	82.0	70.3	78.3	78.2	52.8	25.4
	S^i							5.5	2.4	
70	1	74	78	72	84	77	85			
	2	69	83	69	83	76	80			
	3	74	78	75	87	83	79			
	4	71	80	75	85	79	77			
	$\bar{x}_i$	72.0	79.8	72.8	84.8	78.8	80.3	78.0	52.8	25.2
	S^i							4.9	2.4	
75	1	136	156	150	140	147	141		121	
	2	148	151	154	149	150	147		115	
	3	144	147	158	137	154	137		123	
	4	146	157	150	138	146	146		120	
	$\bar{x}_i$	143.5	152.8	153.0	141.0	149.3	142.8	147.1	119.8	27.3
	S^i							5.3	3.4	

TEST AGENT: SA-2

Angle	Titration	x_1	x_2	x_3	x_4	x_5	x_6	$X_{n,0}$	X_i	X_f
	(milligrams of water)									
80	136	149	140	133	139	152				
	2	140	155	140	146	144	142			
	3	138	149	152	143	137	147			
	4	144	153	147	144	139	147			
	$\overline{x_i}$	139.5	151.5	144.8	141.5	139.8	147.0	144.0	119.8	24.2
	S^i							4.7	3.4	
85	1	154	142	140	146	139	148			
	2	149	147	153	148	144	154			
	3	158	139	147	140	146	142			
	4	155	146	141	146	141	150			
	$\overline{x_i}$	154.0	143.5	145.3	145.0	142.5	148.5	146.5	119.8	26.7
	S^i							4.2	3.4	

TEST AGENT: AC-1

Angle	Titration (milligrams of water)	x_1	x_2	x_3	x_4	x_5	x_6	$X_{n,\Omega}$	X_i	X_f
5	1	267	315	288	302	278	284		156	
	2	270	296	291	297	281	288		148	
	3	271	301	287	298	282	280		146	
	4	274	305	289	297	280	282		152	
	$\bar{x}_i$	270.5	304.3	288.8	298.5	280.3	283.5	287.7	150.5	137.2
	S^i							12.3	4.4	
10	1	305	278	280	294	286	296		208	
	2	300	278	290	296	285	294		201	
	3	301	276	298	296	284	298		203	
	4	299	281	296	293	287	298		207	
	$\bar{x}_i$	301.3	278.3	291.0	294.5	285.5	296.5	291.2	204.8	86.4
	S^i							82.	3.3	
15	1	128	173	135	147	164	147			
	2	129	175	135	149	163	144			
	3	137	178	132	146	168	149			
	4	129	171	131	145	164	151			
	$\bar{x}_i$	130.8	174.3	133.3	146.8	164.8	147.8	149.6	65.6	84.0
	S^i							17.1	1.1	
20	1	120	121	127	117	119	122		40	
	2	118	120	126	119	119	119		41	
	3	118	121	128	117	117	121		41	
	4	119	123	126	116	120	121		39	
	$\bar{x}_i$	118.8	121.3	126.8	117.3	118.8	120.8	120.6	40.3	80.3
	S^i							3.4	1.0	
25	1	146	100	111	109	113	117		36	
	2	145	102	119	105	115	117		39	
	3	141	106	124	107	109	115		37	
	4	144	110	121	104	112	119		39	
	$\bar{x}_i$	144.0	104.5	118.8	106.3	112.3	117.0	117.2	37.8	79.4
	S^i							14.3	1.5	

TEST AGENT: AC-1

Angle	Titration	x_1	x_2	x_3	x_4	x_5	x_6	$X_{n,\theta}$	X_i	X_f
	(milligrams of water)									
30	1	112	133	119	116	121	125			
	2	114	132	120	115	120	124			
	3	113	131	119	116	119	123			
	4	112	133	117	116	121	125			
	$\overline{x}_i$	112.8	132.3	118.8	116.3	120.3	124.3	120.8	40.3	80.5
	S^i							6.8	1.0	
35	1	115	109	137	121	117	112			
	2	117	105	138	123	120	112			
	3	117	113	134	123	109	113			
	4	117	110	139	121	115	117			
	$\overline{x}_i$	116.5	109.3	137.0	122.0	115.3	113.5	118.9	37.8	81.1
	S^i							9.8	1.5	
40	1	60	59	63	59	61	61			
	2	61	59	63	59	63	65			
	3	59	61	61	61	63	63			
	4	61	60	64	63	60	62			
	$\overline{x}_i$	60.3	59.8	62.8	60.5	61.8	62.8	61.3	18.1	43.2
	S^i							1.3	1.1	
45	1	35	39	43	41	33	34			
	2	26	39	44	39	35	32			
	3	38	37	42	38	31	39			
	4	38	40	41	36	36	33			
	$\overline{x}_i$	36.8	38.8	42.5	38.5	33.8	34.5	37.4	18.1	19.3
	S^i							3.2	1.1	
50	1	38	32	39	34	41	34			
	2	34	35	36	39	39	31			
	3	35	34	40	35	36	29			
	4	36	39	39	33	36	29			
	$\overline{x}_i$	35.8	35.0	38.5	35.3	38.0	30.8	35.6	18.1	17.5
	S^i							2.7	1.1	

TEST AGENT: AC-1

Angle	Titration	x_1	x_2	x_3	x_4	x_5	x_6	$X_{n,\Omega}$	X_i	X_f
	(milligrams of water)									
55	1	33	46	45	55	49	51			
	2	35	50	46	53	45	49			
	3	37	50	44	54	48	51			
	4	31	52	49	47	48	47			
	$\bar{x}_i$	34.0	49.5	46.0	52.3	47.5	49.5	46.5	18.1	28.4
	S_i							6.5	2.9	
60	1	46	49	53	53	55	52			
	2	47	50	60	51	52	48			
	3	49	52	63	49	50	51			
	4	45	49	59	50	51	50			
	$\bar{x}_i$	46.8	50.0	61.3	50.8	52.0	50.3	51.9	31.2	20.7
	S_i							4.9	1.0	
65	1	54	64	56	46	51	60			
	2	56	63	54	45	49	58			
	3	57	59	52	49	50	60			
	4	54	64	54	48	52	62			
	$\bar{x}_i$	55.3	62.5	54.0	47.0	50.5	60.0	54.9	31.2	23.7
	S_i							5.8	1.0	
70	1	52	57	54	56	55	63			
	2	46	66	52	54	55	63			
	3	51	54	52	52	51	65			
	4	48	58	54	55	54	62			
	$\bar{x}_i$	49.3	58.8	53.0	54.3	53.8	63.3	55.4	31.2	24.2
	S_i							4.9	1.0	
75	1	58	64	55	46	51	49			
	2	61	67	52	44	56	53			
	3	57	67	52	47	51	51			
	4	55	64	49	48	53	50			
	$\bar{x}_i$	57.8	65.5	52.0	46.3	52.8	50.8	54.2	31.2	23.0
	S_i							6.7	1.0	

TEST AGENT: AC-1

Angle	Titration	x_1	x_2	x_3	x_4	x_5	x_6	$X_{n,\theta}$	X_i	X_f
	(milligrams of water)									
80	1	178	195	149	170	183	137			
	2	172	196	146	162	178	141			
	3	175	189	152	164	186	144			
	4	170	197	156	165	186	140			
	$\bar{x}_i$	173.8	194.3	150.8	165.3	183.3	140.5	168.0	143.2	24.8
	S^i							20.1	5.8	
85	1	198	162	135	186	196	166			
	2	191	153	131	194	198	169			
	3	191	178	138	188	191	164			
	4	182	160	140	186	194	166			
	$\bar{x}_i$	190.5	165.8	136.0	188.5	194.8	166.3	173.7	143.2	30.5
	S^i							22.3	5.8	

TEST AGENT: EE-1

Angle	Titration (milligrams of water)	x_1	x_2	x_3	x_4	x_5	x_6	$X_{n,\theta}$	X_i	X_f
5	1	196	191	194	191	196	192		36	
	2	194	193	191	197	196	193		36	
	3	197	196	196	197	198	198		37	
	4	199	192	196	197	193	200		35	
	$\bar{x}_i$	196.5	193.0	195.8	195.5	195.5	195.8	195.4	36.0	159.4
	S_i							1.2	1.0	
10	1	189	195	191	200	194	197			
	2	191	197	193	202	196	194			
	3	191	198	200	199	192	195			
	4	193	195	200	204	197	196			
	$\bar{x}_i$	191.0	196.0	196.0	201.3	194.8	195.5	195.8	36.0	159.8
	S_i							3.3	1.0	
15	1	178	221	228	222	204	126		100	
	2	187	216	219	231	207	219		102	
	3	193	218	222	229	205	215		104	
	4	185	220	224	227	203	221		104	
	$\bar{x}_i$	185.8	218.8	223.3	227.3	204.8	217.8	213.0	102.5	110.5
	S_i									
20	1	156	139	121	133	144	154			
	2	151	137	125	137	148	152			
	3	153	140	126	136	140	154			
	4	154	135	125	138	153	157			
	$\bar{x}_i$	153.5	137.8	124.3	136.0	146.3	154.3	142.0	102.5	39.5
	S_i							11.6	1.9	
25	1	42	72	78	69	63	66		15	
	2	43	74	86	66	61	63		14	
	3	46	75	80	64	67	67		15	
	4	45	70	79	68	67	61		17	
	$\bar{x}_i$	47.8	72.8	80.8	66.8	64.5	64.3	66.2	15.3	50.9
	S_i							11.0	1.3	

TEST AGENT: EE-1

Angle	Titration	x_1	x_2	x_3	x_4	x_5	x_6	$X_{n,\theta}$	X_i	X_f
30	1	68	59	62	61	53	60			
	2	70	60	55	63	55	63			
	3	66	61	57	59	57	64			
	4	67	63	57	63	56	66			
	$\bar{x}_i$	67.8	60.8	57.8	61.5	55.3	63.3	61.1	15.3	45.8
	S^1							4,3	1.3	
35	1	70	69	69	62	71	68		18	
	2	67	74	62	65	70	66		21	
	3	66	72	59	64	66	66		20	
	4	70	68	61	62	68	63		20	
	$\bar{x}_i$	68.3	70.8	62.8	63.3	68.8	65.8	66.6	19.8	46.8
	S^1							3.2	1.3	
40	1	61	60	67	59	64	62			
	2	63	61	63	61	63	61			
	3	63	63	66	63	61	63			
	4	65	62	68	60	65	60			
	$\bar{x}_i$	63.0	61.5	66.0	60.8	63.3	61.5	62.7	19.8	42.9
	S^1							1.9	1.3	
45	1	65	49	54	50	59	63			
	2	55	58	56	48	58	68			
	3	64	55	58	56	55	64			
	4	63	52	55	55	60	63			
	$\bar{x}_i$	61.8	53.5	55.8	52.3	58.0	64.3	57.6	19.8	37.8
	S^1							4.7	1.3	
50	1	86	81	76	85	83	92		50	
	2	92	80	80	87	85	90		45	
	3	93	83	81	90	85	95		47	
	4	94	79	79	88	88	90		48	
	$\bar{x}_i$	91.3	80.8	79.0	87.5	85.3	91.8	86.0	47.5	38.5
	S^1							5.3	2.1	

TEST AGENT: EE-1

Angle	Titration (milligrams of water)	x_1	x_2	x_3	x_4	x_5	x_6	$X_{n,0}$	X_i	X_f
55	1	92	85	93	99	94	90			
	2	90	88	91	98	96	98			
	3	95	90	91	98	97	91			
	4	91	85	94	95	98	94			
	$\overline{x}_i$	92.0	84.5	92.3	97.5	96.3	93.3	92.7	47.5	45.2
	S^i							4.6	2.1	
60	1	96	101	92	90	90	101			
	2	99	102	91	93	89	101			
	3	99	103	94	95	92	98			
	4	98	98	93	94	95	104			
	$\overline{x}_i$	98.0	101.0	92.5	92.8	91.5	101.0	96.1	47.5	48.6
	S^i							4.4	2.1	
65	1	69	64	74	80	71	74		24	
	2	72	66	74	77	77	72		26	
	3	73	64	72	81	69	77		28	
	4	74	67	75	78	73	71		25	
	$\overline{x}_i$	72.0	65.3	73.8	79.0	72.5	73.5	72.7	25.8	46.9
	S^i							4.4	1.7	
70	1	64	69	74	71	75	65			
	2	63	74	81	67	77	66			
	3	66	69	74	68	76	68			
	4	61	67	77	71	79	69			
	$\overline{x}_i$	63.5	69.8	76.5	69.3	76.8	66.8	70.5	25.8	44.7
	S^i							5.3	1.7	
75	1	68	78	70	68	64	70			
	2	74	81	69	65	63	71			
	3	74	84	70	66	66	67			
	4	67	82	73	66	67	69			
	$\overline{x}_i$	70.8	81.3	70.5	66.3	65.0	69.3	70.5	25.8	44.7
	S^i							5.8	1.7	

TEST AGENT: EE-1

Angle	Titration	x_1	x_2	x_3	x_4	x_5	x_6	$X_{n,\theta}$	X_i	X_f
80	1	83	90	88	100	96	88		42	
	2	86	88	79	92	93	91		43	
	3	84	91	82	94	91	86		41	
	4	82	87	84	96	91	88		44	
	$\bar{x}_i$	83.8	89.0	83.3	95.5	92.8	88.3	88.8	42.5	46.3
	S							4.8	1.3	
85	1	96	85	92	94	84	81			
	2	99	85	94	89	90	83			
	3	94	88	90	89	91	80			
	4	93	90	95	88	90	85			
	$\bar{x}_i$	95.5	87.0	92.8	90.0	88.8	82.3	89.4	42.5	46.9
	S							4.6	1.3	

TEST AGENT: SA-3

Angle	Titration	x_1	x_2	x_3	x_4	x_5	x_6	$X_{n,\theta}$	X_i	X_f
	(milligrams of water)									
5	1	186	162	184	175	168	176		16	
	2	189	174	178	185	172	175		17	
	3	196	169	175	176	170	186		16	
	4	195	167	182	179	165	183		17	
	$\bar{x}_i$	191.5	168.0	182.3	178.8	168.8	180.0	178.2	16.5	161.7
	S^i							8.8	1.0	
10	1	133	169	162	185	165	147			
	2	137	166	163	186	164	156			
	3	137	175	170	176	159	159			
	4	137	161	166	172	157	163			
	$\bar{x}_i$	136.0	167.8	165.3	179.8	161.3	156.3	161.1	16.5	144.6
	S^i							14.6	1.0	
15	1	61	58	90	67	64	70			
	2	58	63	92	64	70	67			
	3	59	64	97	69	68	74			
	4	60	64	95	63	67	65			
	$\bar{x}_i$	58.5	62.3	93.5	65.8	67.3	69.0	69.4	16.5	52.9
	S^i							12.4	1.0	
20	1	49	57	47	52	49	57		37	
	2	50	60	48	49	52	55		37	
	3	51	60	48	51	50	58		37	
	4	51	59	47	53	53	55		39	
	$\bar{x}_i$	50.3	59.0	47.5	51.3	51.0	56.3	52.6	37.5	15.1
	S^i							4.2	1.0	
25	1	58	46	52	52	55	60			
	2	49	47	54	54	52	59			
	3	50	48	52	52	56	58			
	4	48	49	52	55	57	61			
	$\bar{x}_i$	48.8	47.5	52.5	53.3	55.0	62.0	53.2	37.5	15.7
	S^i							5.2	1.0	

TEST AGENT: SA-3

Angle	Titration	x_1	x_2	x_3	x_4	x_5	x_6	$X_{n,\Omega}$	X_i	X_f
30	1	70	60	51	53	57	55			
	2	68	60	49	51	59	52			
	3	67	57	51	53	60	53			
	4	65	61	52	56	56	53			
	$\bar{x}_i$	67.5	59.5	50.8	53.3	58.0	53.3	57.1	37.5	19.6
	S_i							6.1	1.0	
35	1	79	69	89	81	77	70		54	
	2	76	67	85	81	70	69		51	
	3	81	73	87	77	74	74		55	
	4	78	73	90	79	76	72		56	
	$\bar{x}_i$	78.5	70.5	87.8	79.5	74.3	71.3	77.0	54.0	23.0
	S_i							6.4	2.2	
40	1	87	77	76	70	90	81			
	2	83	80	79	75	91	79			
	3	85	74	77	73	94	82			
	4	81	80	81	71	86	77			
	$\bar{x}_i$	84.0	77.8	78.3	72.3	90.3	79.8	80.4	54.0	26.4
	S_i							6.1	2.2	
45	1	70	76	82	88	81	74			
	2	74	71	87	84	77	75			
	3	76	78	83	82	78	73			
	4	77	76	79	83	79	76			
	$\bar{x}_i$	74.3	75.3	82.8	84.3	78.8	74.5	78.3	54.0	24.3
	S_i						4.4	2.2		
50	1	51	66	59	60	70	54		31	
	2	53	67	56	59	68	56		32	
	3	55	63	54	58	69	53		30	
	4	52	65	56	60	65	52		31	
	$\bar{x}_i$	52.8	65.3	56.3	59.3	68.0	53.8	59.3	31.0	28.3
	S_i							6.2	1.0	

TEST AGENT: SA-3

Angle	Titration (milligrams of water)	x_1	x_2	x_3	x_4	x_5	x_6	$X_{n,\theta}$	X_i	X_f
55	1	53	58	51	65	68	57			
	2	53	57	56	66	65	55			
	3	51	56	54	63	64	59			
	4	56	60	54	62	63	60			
	$\overline{x}_i$	53.3	57.8	53.8	64.0	65.0	57.8	58.6	31.0	27.6
	S^i							5.0	1.0	
60	1	59	52	66	61	55	64			
	2	61	52	68	63	57	70			
	3	56	54	64	60	57	68			
	4	57	53	64	59	59	69			
	$\overline{x}_i$	58.3	52.8	65.5	60.8	57.0	67.8	60.4	31.0	29.4
	S^i							5.6	1.0	
65	1	94	102	96	105	106	95		74	
	2	96	99	98	103	102	94		70	
	3	98	101	105	107	105	98		75	
	4	93	98	98	101	100	92		76	
	$\overline{x}_i$	95.3	100.0	99.3	104.0	103.3	94.8	99.5	73.8	25.7
	S^i							3.7	2.6	
70	1	98	106	111	99	101	102			
	2	97	110	113	104	98	99			
	3	99	104	105	98	97	94			
	4	102	105	106	98	96	98			
	$\overline{x}_i$	99.0	106.3	108.8	99.8	98.0	98.3	101.7	73.8	27.9
	S^i							4.6	2.6	
75	1	109	104	98	106	100	98			
	2	106	99	102	109	98	96			
	3	102	105	99	109	102	101			
	4	105	98	96	103	99	100			
	$\overline{x}_i$	105.5	101.5	98.8	106.8	99.8	98.8	101.9	73.8	28.1
	S^i							3.5	2.6	

TEST AGENT: SA-3

Angle	Titration (milligrams of water)	x_1	x_2	x_3	x_4	x_5	x_6	$X_{n,\theta}$	X_i	X_f
80	1	45	39	42	43	41	39		18	
	2	47	42	45	47	39	35		19	
	3	49	43	42	45	38	37		19	
	4	50	42	44	46	37	36		20	
	$\overline{x_i}$	47.8	41.5	43.3	45.3	38.8	36.8	42.3	19.0	23.3
	S^i							4.1	1.0	
85	1	42	41	39	46	47	44			
	2	43	39	39	45	47	45			
	3	43	42	40	44	45	43			
	4	45	42	41	47	44	42			
	$\overline{x_i}$	43.3	41.0	39.8	45.5	45.8	43.5	43.2	19.0	24.2
	S^i							2.4	1.0	